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Sir:

Transmitted herewith for filing is the patent
application of:

Inventor: TA YEN CHING ET AL.

For: POLYMER WITH PENDENT CYCLIC
OLEFINIC FUNCTIONS FOR OXYGEN
SCAVENGING PACKAGING

Case Docket No. T-5505
Chevron Corporation
Law Department - Patent and Licensing Unit
P. O. Box 7141
San Francisco, CA 94120-7141

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Date of Deposit July 31, 1998

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W. Brad Haymond
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Enclosed are:

- ☒ Specification [Total Pages = 75].
- ☐ An Assignment of the invention to **Chevron Chemical Company LLC**, San Francisco, CA, a corporation of Delaware.
- ☐ A certified copy of a _____ application.
- ☒ Drawing(s) [Total Sheets = 4].
- ☐ Combined Oath or Declaration and Power of Attorney [Total Pages = ____].
 - ☐ Newly executed (original or copy)
 - ☐ Copy from a prior application (37 CFR §1.63(d)) (for continuation/divisional)
 - ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
- ☐ Incorporation by Reference (*useable if copy of Oath or Declaration from prior application is being submitted*)
The entire disclosure of the prior application, from which a copy of the oath or declaration is being supplied, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
- ☐ Information Disclosure Statement.
- ☐ If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:
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	(Col. 1)	(Col. 2)
For	No. Filed	No. Extra
Basic Application Fee		
Total claims	98 - 20	78
Independent claims	5 - 3	2
<input type="checkbox"/> Multiple dependent claims presented		

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Rate	Fee
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WBHaymond:kmw
Enclosures

July 31, 1998

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A
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1 BE IT KNOWN, that We, TA YEN CHING, a citizen of the United States of
2 America, resident of Novato, County of Marin, State of California; JOSEPH L.
3 GOODRICH, a citizen of the United States of America, resident of Lafayette,
4 County of Contra Costa, State of California; JAMES P. LEONARD, a citizen of
5 the United States of America, resident of San Rafael, County of Marin, State
6 of California; and KENNETH W. RUSSELL, a citizen of the United States of
7 America, resident of Orange, County of Orange, State of Texas, have
8 invented new and useful improvements in a

9 **POLYMER WITH PENDENT CYCLIC OLEFINIC FUNCTIONS**
10 **FOR OXYGEN SCAVENGING PACKAGING**

1 **POLYMER WITH PENDENT CYCLIC OLEFINIC FUNCTIONS**
2 **FOR OXYGEN SCAVENGING PACKAGING**

3 FIELD OF THE INVENTION

4 The present invention relates to compositions for use in areas such as food
5 packaging, and with minimal effect on odor and taste of packaged contents.
6 The invention preferably uses ethylene acrylate copolymers which are
7 modified with selected cyclic allylic pendent groups for use in oxygen
8 scavenging packaging materials.

9 BACKGROUND OF THE INVENTION

10 New polymer compositions having properties that are particularly tailored for
11 specific applications are required in response to more specific and
12 sophisticated end uses. It can be difficult to make these compositions directly
13 by polymerization from monomers or via solution esterification or
14 transesterification, but manufacturing them in melt mixing equipment such as
15 an extruder has provided an efficient, economical and viable means to supply
16 increasingly complex polymers to meet the needs in specialized markets.

17 It is well known that regulating the exposure of oxygen-sensitive products to
18 oxygen maintains and enhances the quality and "shelf-life" of the product. For
19 instance, by limiting the exposure of oxygen sensitive food products to oxygen
20 in a packaging system, the quality or freshness of food is maintained, spoilage
21 reduced and the food shelf life extended. In the food packaging industry,
22 several means for regulating oxygen exposure have already been developed.
23 These means include modified atmosphere packaging (MAP) and oxygen
24 barrier film packaging.

25 One method currently being used is "active packaging", whereby the package
26 containing the food product has been modified in some manner to regulate

1 the food's exposure to oxygen. One form of active packaging uses oxygen-
2 scavenging sachets which contain a composition which scavenges the
3 oxygen through oxidation reactions. One type of sachet contains iron-based
4 compositions which oxidize to their ferric states. Another type of sachet
5 contains unsaturated fatty acid salts on a particulate adsorbent. Yet another
6 sachet contains metal/polyamide complex. However, one disadvantage of
7 sachets is the need for additional packaging operations to add the sachet to
8 each package. A further disadvantage arising from the iron-based sachets is
9 that certain atmospheric conditions (e.g., high humidity, low CO₂ level) in the
10 package are sometimes required in order for scavenging to occur at an
11 adequate rate. Further, the sachets can present a problem to consumers if
12 accidentally ingested.

13 Another means for regulating exposure of a packaged product to oxygen
14 involves incorporating an oxygen scavenger into the packaging structure
15 itself. A more uniform scavenging effect through the package is achieved by
16 incorporating the scavenging material in the package instead of adding a
17 separate scavenger structure (e.g., a sachet) to the package. This may be
18 especially important where there is restricted airflow inside the package. In
19 addition, incorporating the oxygen scavenger into the package structure
20 provides a means of intercepting and scavenging oxygen as it permeates the
21 walls of the package (herein referred to as an "active oxygen barrier"), thereby
22 maintaining the lowest possible oxygen level in the package.

23 One attempt to prepare an oxygen-scavenging wall involves the incorporation
24 of inorganic powders and/or salts. However, incorporation of these powders
25 and/or salts causes reduction of the wall's optical transparency, discoloration
26 after oxidation, and reduced mechanical properties such as tear strength. In
27 addition, these compounds can lead to processing difficulties, especially when
28 fabricating thin films. The oxidation products may migrate into food at levels
29 which would not be regarded as safe or can impart unacceptable taste or
30 smell to food.

1 An oxygen-scavenging composition comprising a blend of a first polymeric
2 component comprising a polyolefin is known, the first polymeric component
3 having been grafted with an unsaturated carboxylic anhydride or an
4 unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a
5 second polymeric component having -OH, -SH, or -NHR² groups where R² is
6 H, C₁-C₃ alkyl, substituted C₁-C₃ alkyl; and a catalytical amount of metal salt
7 capable of catalyzing the reaction between oxygen and the second polymeric
8 component, the polyolefin being present in an amount sufficient so that the
9 blend is not phase-separated. A blend of polymers is utilized to obtain oxygen
10 scavenging, and the second polymeric component is preferably a polyamide
11 or a copolyamide such as the copolymer of m-xylylene-diamine and adipic
12 acid (MXD6).

13 Some oxygen scavenging systems produce an oxygen-scavenging wall. This
14 is done by incorporating a metal catalyst-polyamide oxygen scavenging
15 system into the package wall. Through catalyzed oxidation of the polyamide,
16 the package wall regulates the amount of oxygen which reaches the interior
17 volume of the package (active oxygen barrier) and has been reported to have
18 oxygen scavenging rate capabilities up to about 5 cubic centimeters (cc)
19 oxygen per square meter per day at ambient conditions. However, this
20 system suffers from significant disadvantages.

21 One particularly limiting disadvantage of polyamide/catalyst materials can be
22 a low oxygen scavenging rate. Adding these materials to a high-barrier
23 package containing air can produce a package which is not generally suitable
24 for creating an internal oxygen level of less than 0.1% within seven days at
25 storage temperatures, as is typically required for headspace oxygen
26 scavenging applications.

27 There are also disadvantages to having the oxygen-scavenging groups in the
28 backbone or network structure in this type of polyamide polymer. The basic
29 polymer structure can be degraded and weakened upon reaction with oxygen.

1 This can adversely affect physical properties such as tensile or impact
2 strength of the polymer. The degradation of the backbone or network of the
3 polymer can further increase the permeability of the polymer to those
4 materials sought to be excluded, such as oxygen.

5 Moreover, polyamides previously used in oxygen scavenging materials, such
6 as MXD6, are typically incompatible with thermoplastic polymers used in most
7 flexible packaging walls, such as ethylene-vinyl acetate copolymers and low
8 density polyethylene. Even further, when such polyamides are used by
9 themselves to make a flexible package wall, they may result in inappropriately
10 stiff structures. They also incur processing difficulties and higher costs when
11 compared with the costs of thermoplastic polymers typically used to make
12 flexible packaging. Even further, they are difficult to heat seal. Thus, all of
13 these are factors to consider when selecting materials for packages,
14 especially multi-layer flexible packages and when selecting systems for
15 reducing oxygen exposure of packaged products.

16 Another approach to scavenging oxygen is an oxygen-scavenging
17 composition comprising an ethylenically unsaturated hydrocarbon and a
18 transition metal catalyst. Ethylenically unsaturated compounds such as
19 squalene, dehydrated castor oil, and 1,2-polybutadiene are useful oxygen
20 scavenging compositions, and ethylenically saturated compounds such as
21 polyethylene and ethylene copolymers are used as diluents. Compositions
22 utilizing squalene, castor oil, or other such unsaturated hydrocarbon typically
23 have an oily texture as the compound migrates toward the surface of the
24 material. Further, polymer chains which are ethylenically unsaturated in the
25 backbone would be expected to degrade upon scavenging oxygen,
26 weakening the polymer due to polymer backbone breakage, and generating a
27 variety of off-odor/off-taste by-products.

28 Other oxidizable polymers recognized in the art include "highly active"
29 oxidizable polymers such as poly(ethylene-methyl acrylate-benzyl acrylate),

1 EMBZ, and poly(ethylene-methyl acrylate-tetrahydrofurfuryl acrylate), EMTF,
2 as well as poly(ethylene-methyl acrylate-nopol acrylate), EMNP. Although
3 effective as oxygen scavengers, these polymers have the drawback of giving
4 off large amounts of volatile by-products and/or strong odors after oxygen
5 scavenging.

6 Also known are oxygen-scavenging compositions which comprise a transition-
7 metal salt and a compound having an ethylenic backbone and having allylic
8 pendent or terminal moieties which contain a carbon atom that can form a free
9 radical that is resonance-stabilized by an adjacent group. Such a polymer
10 needs to contain a sufficient amount and type of transition metal salt to
11 promote oxygen scavenging by the polymer when the polymer is exposed to
12 an oxygen-containing fluid such as air. Although effective as oxygen
13 scavengers, upon oxidation, we have found that allylic pendent groups on an
14 ethylenic backbone tend to generate considerable amounts of organic
15 fragments. We believe this is a result of oxidative cleavage. We believe
16 these fragments can interfere with the use of allylic pendent groups as oxygen
17 scavengers in food packaging.

18 The present invention solves many of the problems of the prior art, especially
19 with an oxygen scavenging packaging material incorporating polymers
20 comprising cyclic allylic (olefinic) pendent groups which produce little or no
21 migration of oxidation by-products adversely affecting odor or taste, thus
22 minimizing organoleptic problems in food packaging. This is because the
23 cyclic allylic structures are less likely to fragment or cleave after oxidation than
24 the conventional open chain allylic (olefinic) groups used in oxygen
25 scavenging packaging material.

SUMMARY OF THE INVENTION

2 According to the present invention, a composition is provided comprising a
3 polymeric backbone, cyclic olefinic pendent groups and linking groups linking
4 the olefinic pendent groups to the polymeric backbone.

5 Also according to the present invention, an oxygen scavenging composition is
6 provided comprising a polymeric backbone, cyclic olefinic pendent groups,
7 linking groups linking the olefinic pendent groups to the polymeric backbone
8 and a transition metal catalyst.

9 Also according to the present invention, an article of manufacture is provided
10 which is suitable as a container, the container inhibiting oxidation of contents
11 of the container by removing oxygen from the container and by inhibiting
12 ingress of oxygen into the container from outside the container, the article
13 comprising an oxygen scavenging composition which comprises a polymeric
14 backbone, cyclic olefinic pendent groups, linking groups linking the olefinic
15 pendent groups to the backbone, and a transition metal catalyst.

16 Also according to the present invention, a layer suitable for scavenging
17 oxygen is provided which comprises (a) a polymer backbone; (b) cyclic
18 olefinic pendent groups; (c) linking groups linking the backbone with the
19 pendent groups; and (d) a transition metal catalyst.

20 Also according to the present invention, a process of making a polymer
21 material is provided, the process being selected from the group consisting of
22 esterification, transesterification, amidation, transamidation and direct
23 polymerization, in which the oxygen scavenging packaging material
24 comprises a polymer backbone, cyclic olefinic pendent groups, linking groups
25 linking the backbone with the pendent groups.

1 In a preferred embodiment of the invention, the polymeric backbone of the
2 above compositions, article, layer and process is ethylenic and the linking
3 groups are selected from the group consisting of:

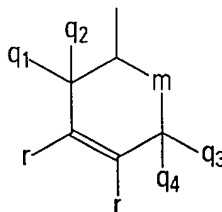
4 $-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;

5 $-(C=O)-NH-(CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

6 wherein R is hydrogen or an alkyl group selected from the group consisting of
7 methyl, ethyl, propyl and butyl groups and where n is an integer in the range
8 from 1 to 12.

9 In a more preferred embodiment of the invention, the cyclic olefinic pendent
10 groups of the above compositions, article, layer and process have the
11 structure (I):

12 (I)



15 where q1, q2, q3, q4, and r are selected from the group consisting of -H, -CH3,
16 and -C2H5; and where m is $-(CH_2)_n-$ with n being an integer in the range from
17 0 to 4; and wherein, when r is -H, at least one of q1, q2, q3 and q4 is -H.

18 In another preferred embodiment of the invention, the polymeric backbone of
19 the above compositions, article, layer and process comprises monomers
20 selected from the group consisting of ethylene and styrene.

21 In yet another preferred embodiment of invention, the cyclic olefinic pendent
22 groups of the above compositions, article, layer and process are grafted onto

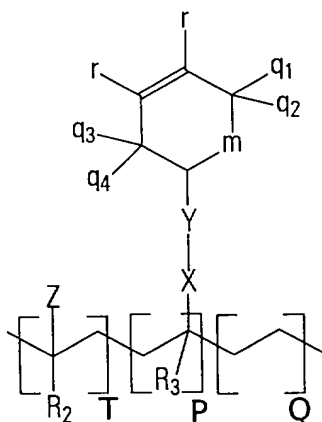
1 the linking groups of the polymeric backbone by a esterification,
2 transesterification, amidation or transamidation reaction.

3 In still another preferred embodiment of the invention, the esterification,
4 transesterification, amidation or transamidation reaction of the above
5 compositions, article, layer and process is a solution reaction or a reactive
6 extrusion.

7 In another preferred embodiment of the invention, the esterification,
8 transesterification, amidation or transamidation reaction of the above
9 compositions, article, layer and process is catalyzed by a catalyst selected
10 from the group consisting of strong non-oxidizing acids, tertiary amines,
11 Group I alkoxides, Group IVB alkoxides, and Group IVA organometallics.

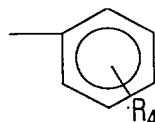
12 In yet another preferred embodiment of invention, the catalyst of the above
13 compositions, article, layer and process is selected from a group consisting of
14 toluene sulfonic acid, sodium methoxide, tetrabutyl titanate, tetraisopropyl
15 titanate, tetra-n-propyl-titanate, tetraethyl titanate, 2-hydroxy-pyridine and
16 dibutyltin dilaurate.

17 In still another preferred embodiment of the invention, the polymeric
18 backbone, linking groups and cyclic olefin pendent groups of the above
19 compositions, article, layer and process comprise repeating units, each unit
20 having a structure (II) as follows:



(II)

wherein P+T+ Q is 100 mol % of the total composition; P is greater than 0 mol % of the total composition; Z is selected from the group consisting of an aryl group; $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group:



where R_4 is selected from the group consisting of $-CH_3$, $-C_2H_5$, and $-H$; R_1 is selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$ and $-C_4H_9$; R_2 and R_3 are selected from the group consisting of $-H$ and $-CH_3$; X is selected from the group consisting of $-O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$, $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell-$; ℓ is an integer in the range from 1 to 6; Y is $-(CHR)_n-$, where n is an integer in the range from 0 to 12, R being selected from the group consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in the range from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is $-H$.

1 In another preferred embodiment of the invention, the cyclic olefinic pendent
2 groups of the above compositions, article, layer and process are selected
3 from the group consisting of cyclohexene-4-methylene radical, 1-methyl
4 cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-methylene radical,
5 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl cyclohexene-4-
6 methylene radical, 1,5-dimethyl cyclohexene-4-methylene radical,
7 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-
8 methylene radical, cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-
9 ethylene radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl
10 cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical,
11 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-
12 ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical, cyclohexene-
13 4-propylene radical, 1-methyl cyclohexene-4-propylene radical, 2-methyl
14 cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-propylene radical,
15 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl cyclohexene-4-
16 propylene radical, 2,5-dimethyl cyclohexene-4-propylene radical,
17 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-methylene
18 radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-
19 methylene radical, 1,2-dimethyl cyclopentene-4-methylene radical,
20 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
21 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical,
22 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
23 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl
24 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,
25 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-
26 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
27 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene
28 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
29 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
30 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene
31 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl
32 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene

1 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and

2 1,2,3,5-tetramethyl cyclopentene-4-propylene radical.

3 In yet another preferred embodiment of the invention, the composition of the

4 above compositions, article, layer and process is a ethylene/methyl

5 acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl

6 acrylate/ethylene copolymer, a cyclohexenyl methyl methacrylate/styrene

7 copolymer, a cyclohexenyl methyl acrylate homopolymer or a methyl

8 acrylate/cyclohexenyl methyl acrylate copolymer.

9 In another preferred embodiment of the invention, the odor and taste

10 characteristics of products packaged with material comprised of the above

11 compositions, article, layer and process are not adulterated as a result of

12 oxidation of the composition.

13 In still another preferred embodiment of the invention, there is no significant

14 fragmentation of the olefinic pendent groups and linking groups from the

15 polymeric backbone as a result of oxidation of the above compositions, article,

16 layer and process.

17 In yet another preferred embodiment of the invention, the transition metal

18 catalyst of the above oxygen scavenging composition, article of manufacture,

19 layer and process is a metal salt.

20 In still another preferred embodiment of the invention, the metal in the metal

21 salt of the above oxygen scavenging composition, article of manufacture,

22 layer and process is cobalt.

23 In still another preferred embodiment of the invention, the metal salt of the

24 above oxygen scavenging composition, article of manufacture, layer and

25 process is selected from the group consisting of cobalt neodecanoate, cobalt

26 2-ethylhexanoate, cobalt oleate and cobalt stearate.

1 In yet another preferred embodiment of the invention, the composition of the
2 above oxygen scavenging composition, article of manufacture, layer and
3 process further comprises at least one triggering material to enhance initiation
4 of oxygen scavenging.

5 In still another preferred embodiment of the invention, the triggering material
6 of the above oxygen scavenging composition, article of manufacture, layer
7 and process is a photo initiator.

8 In a preferred embodiment of the invention, the above article of manufacture
9 is a package.

10 In another preferred embodiment of invention, the package article of the
11 above article of manufacture comprises a flexible film having a thickness of at
12 most 10 mil or a flexible sheet having a thickness of at least 10 mil.

13 In yet another preferred embodiment of the invention, the oxygen scavenging
14 system of the package article of the above article of manufacture comprises at
15 least one additional layer selected from among oxygen barrier layers,
16 polymeric selective layers, and heat seal layers.

17 In still another preferred embodiment of the invention, the above article of
18 manufacture is a package with a food product located within the package.

19 In yet another preferred embodiment of the invention, the above article of
20 manufacture is a package for packaging a cosmetic, chemical, electronic
21 device, pesticide or a pharmaceutical composition.

22 In still another preferred embodiment of the invention, a multi-layer film
23 comprises the article of the above article of manufacture and the film has at
24 least one additional functional layer.

1 In yet another preferred embodiment of the invention, the multi-layer film of
2 the above article of manufacture has at least one additional layer selected
3 from among oxygen barrier layers, polymeric selective barrier layers,
4 structural layers and heat seal layers.

5 In still another preferred embodiment of the invention, the multi-layer film of
6 the above article of manufacture has at least one additional layer which is an
7 oxygen barrier layer.

8 In yet another preferred embodiment of the invention, the multi-layer film of
9 the above article of manufacture further comprises at least one polymeric
10 selective barrier layer.

11 In still another preferred embodiment of the invention, the multi-layer film of
12 the above article of manufacture further comprises at least one heat seal
13 layer.

14 In yet another preferred embodiment of the invention, the multi-layer film of
15 the above article of manufacture further comprises at least one structural
16 layer.

17 In still another preferred embodiment of the invention, the above article of
18 manufacture is a rigid container, sealing gasket, patch, container closure
19 device, bottle cap, bottle cap insert or molded or thermoformed shape.

20 In yet another preferred embodiment of the invention, the molded or
21 thermoformed shape of the above article of manufacture is a bottle or tray.

22 In still another preferred embodiment of the invention, the above layer in
23 addition comprises polymeric diluent.

24 In yet another preferred embodiment of the invention, the diluent of the above
25 layer is a thermoplastic polymer.

- 1 In still another preferred embodiment of the invention, the above layer is
2 adjacent to one or more additional layers.
- 3 In still another preferred embodiment of the invention, at least one of the
4 additional layers adjacent to the above layer is an oxygen barrier.
- 5 In still another preferred embodiment of the invention, the oxygen barrier of
6 the above layer comprises a member of the group consisting of poly(ethylene-
7 vinyl alcohol), polyacrylonitrile, poly(vinyl chloride), polyamides,
8 poly(vinylidene dichloride), poly(ethylene terephthalate), silica, metal foil and
9 metalized polymeric films.
- 10 In still another preferred embodiment of the invention, the one or more of said
11 additional layer or layers of the above layer is coextruded with the above
12 layer.
- 13 In yet another preferred embodiment of the invention, the one or more of said
14 additional layer or layers of the above layer is laminated onto the above layer.
- 15 In still another preferred embodiment of the invention, the one or more of said
16 additional layer or layers of the above layer is coated onto the above layer.
- 17 In yet another preferred embodiment of the invention, the above layer is
18 flexible.
- 19 In still another preferred embodiment of the invention, the above layer is
20 transparent.
- 21 In yet another preferred embodiment of the invention, an article for packaging
22 wherein the article comprises the above layer.
- 23 In yet another preferred embodiment of the invention, the above process of
24 making the oxygen scavenging packaging material comprises the steps of:

- 1 (a) selecting polymers from the group consisting of styrene/maleic
2 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
3 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
4 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
5 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,
6 and styrene/methyl methacrylate to form a mixture and combining the
7 polymers with an esterifying/transesterifying compound selected from
8 the group consisting of cyclohexene-4-methanol, 1-methyl cyclohexene-
9 4-methanol, 2-methyl cyclohexene-4-methanol, 5-methyl cyclohexene-4-
10 methanol, 1,2-dimethyl cyclohexene-4-methanol, 1,5-dimethyl
11 cyclohexene-4-methanol, 2,5-dimethyl cyclohexene-4-methanol,
12 1,2,5-trimethyl cyclohexene-4-methanol, cyclohexene-4-ethanol,
13 1-methyl cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol,
14 5-methyl cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol,
15 1,5-dimethyl cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-
16 ethanol, 1,2,5-trimethyl cyclohexene-4-ethanol, cyclohexene-4-propanol,
17 1-methyl cyclohexene-4-propanol, 2-methyl cyclohexene-4-propanol,
18 5-methyl cyclohexene-4-propanol, 1,2-dimethyl cyclohexene-4-propanol,
19 1,5-dimethyl cyclohexene-4-propanol, 2,5-dimethyl cyclohexene-4-
20 propanol, 1,2,5-trimethyl cyclohexene-4-propanol, cyclopentene-4-
21 methanol, 1-methyl cyclopentene-4-methanol, 3-methyl cyclopentene-4-
22 methanol, 1,2-dimethyl cyclopentene-4-methanol, 3,5-dimethyl
23 cyclopentene-4-methanol, 1,3-dimethyl cyclopentene-4-methanol,
24 2,3-dimethyl cyclopentene-4-methanol, 1,2,3-trimethyl cyclopentene-4-
25 methanol, 1,2,3,5-tetramethyl cyclopentene-4-methanol, cyclopentene-4-
26 ethanol, 1-methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-
27 ethanol, 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl
28 cyclopentene-4-ethanol, 1,3-dimethyl cyclopentene-4-ethanol,
29 2,3-dimethyl cyclopentene-4-ethanol, 1,2,3-trimethyl cyclopentene-4-
30 ethanol, 1,2,3,5-tetramethyl cyclopentene-4-ethanol, cyclopentene-4-
31 propanol, 1-methyl cyclopentene-4-propanol, 3-methyl cyclopentene-4-
32 propanol, 1,2-dimethyl cyclopentene-4-propanol, 3,5-dimethyl

- 1 cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-4-propanol,
2 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl cyclopentene-4-
3 propanol, and 1,2,3,5-tetramethyl cyclopentene-4-propanol;
- 4 (b) heating the polymers and esterifying/transesterifying compounds
5 selected in (a) to form a polymer melt;
- 6 (c) processing the melt in an extruder under esterification/transesterification
7 conditions with esterification/transesterification catalysts and
8 antioxidants protecting the melt from oxidation during extrusion, so that
9 the polymer melt undergoes esterification of polymeric anhydrides with
10 cyclic olefin pendent groups, esterification of polymeric acids with cyclic
11 olefin pendent groups or exchange of alkyl groups of polymeric esters
12 with cyclic olefin pendent groups; and
- 13 (d) removing volatile organic products and by-products from the melt.
- 14 In still another preferred embodiment of the invention, the above process of
15 making the oxygen scavenging packaging material comprises the steps of:
- 16 (a) selecting polymers from the group consisting of styrene/maleic
17 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
18 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
19 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
20 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,
21 and styrene/methyl methacrylate to form a mixture and combining the
22 polymers with an amidizing/transamidizing compound selected from the
23 group consisting of cyclohexene-4-methyl amine, 1-methyl cyclohexene-
24 4-methyl amine, 2-methyl cyclohexene-4-methyl amine, 5-methyl
25 cyclohexene-4-methyl amine, 1,2-dimethyl cyclohexene-4-methyl amine,
26 1,5-dimethyl cyclohexene-4-methyl amine, 2,5-dimethyl cyclohexene-4-
27 methyl amine, 1,2,5-trimethyl cyclohexene-4-methyl amine,

- 1 cyclohexene-4-ethyl amine, 1-methyl cyclohexene-4-ethyl amine,
2 2-methyl cyclohexene-4-ethyl amine, 5-methyl cyclohexene-4-ethyl
3 amine, 1,2-dimethyl cyclohexene-4-ethyl amine, 1,5-dimethyl
4 cyclohexene-4-ethyl amine, 2,5-dimethyl cyclohexene-4-ethyl amine,
5 1,2,5-trimethyl cyclohexene-4-ethyl amine, cyclohexene-4-propyl amine,
6 1-methyl cyclohexene-4-propyl amine, 2-methyl cyclohexene-4-propyl
7 amine, 5-methyl cyclohexene-4-propyl amine, 1,2-dimethyl cyclohexene-
8 4-propyl amine, 1,5-dimethyl cyclohexene-4-propyl amine, 2,5-dimethyl
9 cyclohexene-4-propyl amine, 1,2,5-trimethyl cyclohexene-4-propyl
10 amine, cyclopentene-4-methyl amine, 1-methyl cyclopentene-4-methyl
11 amine, 3-methyl cyclopentene-4-methyl amine, 1,2-dimethyl
12 cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl
13 amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl
14 cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-methyl
15 amine, 1,2,3,5-tetramethyl cyclopentene-4-methyl amine, cyclopentene-
16 4-ethyl amine, 1-methyl cyclopentene-4-ethyl amine, 3-methyl
17 cyclopentene-4-ethyl amine, 1,2-dimethyl cyclopentene-4-ethyl amine,
18 3,5-dimethyl cyclopentene-4-ethyl amine, 1,3-dimethyl cyclopentene-4-
19 ethyl amine, 2,3-dimethyl cyclopentene-4-ethyl amine, 1,2,3-trimethyl
20 cyclopentene-4-ethyl amine, 1,2,3,5-tetramethyl cyclopentene-4-ethyl
21 amine, cyclopentene-4-propyl amine, 1-methyl cyclopentene-4-propyl
22 amine, 3-methyl cyclopentene-4-propyl amine, 1,2-dimethyl
23 cyclopentene-4-propyl amine, 3,5-dimethyl cyclopentene-4-propyl
24 amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-dimethyl
25 cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-propyl
26 amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl amine;
- 27 (b) heating the polymers and amidizing/transamidizing compounds selected
28 in (a) to form a polymer melt;
- 29 (c) processing the melt in an extruder under amidation/transamidation
30 conditions with amidation/transamidation catalysts and antioxidants

1 protecting the melt from oxidation during extrusion, so that the polymer
2 melt undergoes amidation of polymeric anhydrides with cyclic olefin
3 pendent groups, amidation of polymeric acids with cyclic olefin pendent
4 groups or exchange of alkyl groups of polymeric esters with cyclic olefin
5 pendent groups; and

6 (d) removing volatile organic products and by-products from the melt.

7 In yet another preferred embodiment of the invention, the above process of
8 making of the oxygen scavenging packaging material comprises the steps of:

9 (a) adding to an autoclave, ethylene and a vinyl monomer comprising a
10 pendent cyclohexene;

11 (b) stirring the ethylene and the vinyl monomer in the autoclave to achieve a
12 mixture;

13 (c) adding a polymerization initiator before, during or after the stirring step;

14 (d) polymerizing the mixture to achieve a polymer; and

15 (e) isolating and purifying the polymer.

16 In still another embodiment of the invention, in the above process, in step (a),
17 an alpha-olefin is added to the autoclave along with the ethylene and the vinyl
18 monomer and, in step (b), the alpha-olefin is stirred with the ethylene and the
19 vinyl monomer to achieve the mixture.

1 DESCRIPTION OF THE DRAWINGS

2 Figure 1 is a schematic showing the overall process leading to the
3 transesterification of ethylene methyl acrylate copolymers (EMAC) to give
4 modified EMAC having cyclic pendent olefins.

5 Figure 2 is a graph comparatively plotting percent oxygen in headspace at
6 4°C (initially at 1% oxygen) against time in days for two 3-layer film extrusions
7 based on Dowlex® 3010/EMCM/Dowlex® 3010 films (EMCM being an
8 acronym for ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer
9 also referred to as poly(ethylene/methyl acrylate/cyclohexene-methyl
10 acrylate)), both including the EMCM inner layer and one of them having
11 50 ppm of a non-volatile antioxidant Irganox® 1010 in the EMCM layer and
12 one of them having 100 ppm Irganox® 1010 in the EMCM layer.

13 Figure 3 is a graph comparatively plotting percent oxygen in headspace at
14 4°C (initially at 1% oxygen) against time in days for an EMCM film and two
15 EBAC blended EMCM films, one of them having 3:1 EBAC:EMCM and one of
16 them having 1:1 EBAC:EMCM.

17 Figure 4 is a graph comparatively plotting the oxygen scavenging rates and
18 capacities at 25°C in which the initial headspace oxygen was 21% (air) for an
19 EMCM film and a 2:1 EBAC:EMCM film.

20 Figure 5 is a graph showing the taste ratings in a comparative taste test
21 between food stored in two oxygen scavenging packages (EMCM and SBS)
22 and a control package (no oxygen scavenger).

23 DETAILED DESCRIPTION OF THE INVENTION

24 This invention relates to an oxygen scavenging polymer composition
25 comprising cyclic allylic pendent groups which can be used in oxygen

1 scavenging packaging material which have either no or low volatile oxidation
2 by-products. Minimizing volatile by-products reduces the problem of
3 organoleptics in oxygen scavenging food packaging.

4 The polymer composition with cyclic allylic pendent groups can be made by
5 grafting methyl cyclohex-1-ene-4-methanol, cyclohex-1-ene-4-methanol
6 (1,2,5,6-tetrahydrobenzyl alcohol) and cyclohex-1-ene-4-propanol onto EMAC
7 resins by transesterification of the corresponding alcohols or transamidation of
8 the corresponding amines with the methyl esters on EMAC to give modified
9 EMAC having pendent cyclic olefins (see Figure 1). The composition can also
10 be made by direct polymerization.

11 The esterification, transesterification, amidation or transamidation reaction
12 can be a solution reaction or by reactive extrusion. The catalysts can be any
13 one of strong non-oxidizing acids, tertiary amines, Group I alkoxides,
14 Group IVB alkoxides and Group IVA metal organics. The level of olefin in the
15 final products can be controlled by the level of transesterification and the
16 methyl ester content of the start EMAC. The molecular weight of the
17 polymers largely depends on the molecular weight of the EMAC feeds.

18 In a preferred embodiment, these products are combined with a transition-
19 metal salt to catalyze the oxygen scavenging properties of the materials. A
20 transition-metal salt, as the term is used here, comprises an element chosen
21 from the first, second and third transition series of the periodic table of the
22 elements, particularly one that is capable of promoting oxidation reactions.
23 This transition-metal salt is in a form which facilitates or imparts scavenging of
24 oxygen by the composition of this invention. A plausible mechanism, not
25 intended to place limitations on this invention, is that the transition element
26 can readily inter-convert between at least two oxidation states and facilitates
27 formation of free radicals. Suitable transition-metal elements include, but are
28 not limited to, manganese II or III, iron II or III, cobalt II or III, nickel II or III,
29 copper I or II, rhodium II, III or IV, and ruthenium. The oxidation state of the

1 transition-metal element when introduced into the composition is not
2 necessarily that of the active form. It is only necessary to have the transition-
3 metal element in its active form at or shortly before the time that the
4 composition is required to scavenge oxygen. The transition-metal element is
5 preferably iron, nickel or copper, more preferably manganese and most
6 preferably cobalt.

7 Suitable counter-ions for the transition metal element are organic or inorganic
8 anions. These include, but are not limited to, chloride, acetate, stearate,
9 oleate, palmitate, 2-ethylhexanoate, citrate, glycolate, benzoate,
10 neodecanoate or naphthenate. Organic anions are preferred. Particularly
11 preferable salts include cobalt 2-ethylhexanoate, cobalt benzoate, cobalt
12 stearate, cobalt oleate and cobalt neodecanoate. The transition-metal
13 element may also be introduced as an ionomer, in which case a polymeric
14 counter-ion is employed.

15 The composition of the present invention when used in forming a oxygen
16 scavenging packaging article can be composed solely of the above described
17 polymer and transition metal catalyst. However, components, such as
18 photoinitiators, can be added to further facilitate and control the initiation of
19 oxygen scavenging properties. For instance, it is often preferable to add a
20 photoinitiator, or a blend of different photoinitiators, to the oxygen scavenger
21 compositions, especially when antioxidants are included to prevent premature
22 oxidation of that composition during processing.

23 Suitable photoinitiators are well known in the art. Such photoinitiators are
24 discussed in U.S. Patent No. 5,211,875. It is also discussed in U.S. Patent
25 Application Serial No. 08/857,325, in which some of the present inventors
26 were contributing inventors and which is incorporated herein by reference.
27 Specific examples include, but are not limited to, benzophenone, o-methoxy-
28 benzophenone, acetophenone, o-methoxy-acetophenone,
29 acenaphthenequinone, methyl ethyl ketone, valerophenone, hexanophenone,

1 α -phenyl-butyrophenone, p-morpholinopropiophenone, dibenzosuberone,
2 4-morpholinobenzophenone, benzoin, benzoin methyl ether,
3 4-o-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone,
4 4'-methoxyacetophenone, substituted and unsubstituted anthraquinones,
5 α -tetralone, 9-acetylphenanthrene, 2-acetyl-phenanthrene,
6 10-thioxanthenone, 3-acetyl-phenanthrene, 3-acetylindole, 9-fluorenone,
7 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one,
8 7-H-benz[de]anthracen-7-one, benzoin tetrahydropyranyl ether,
9 4,4'-bis(dimethylamino)-benzophenone, 1'-acetoneaphthone,
10 2'-acetoneaphthone, acetoneaphthone and 2,3-butanedione,
11 benz[a]anthracene-7,12-dione, 2,2-dimethoxy-2-phenylacetophenone,
12 α,α -diethoxy-acetophenone, α,α -dibutoxyacetophenone, etc. Singlet oxygen
13 generating photosensitizers such as Rose Bengal, methylene blue, and
14 tetraphenyl porphine may also be employed as photoinitiators. Polymeric
15 initiators include polyethylene carbon monoxide and oligo[2-hydroxy-2-methyl-
16 1-[4-(1-methylvinyl)phenyl]propanone]. Use of a photoinitiator is preferable
17 because it generally provides faster and more efficient initiation.

18 When a photoinitiator is used, its primary function is to enhance and facilitate
19 the initiation of oxygen scavenging upon exposure to radiation. The amount
20 of photoinitiator can vary. In many instances, the amount will depend on the
21 amount and type of oxygen scavenging polymer in the present invention, the
22 wavelength and intensity of radiation used, the nature and amount of
23 antioxidants used, as well as the type of photoinitiator used. The amount of
24 photoinitiator also depends on how the scavenging composition is used. For
25 instance, if the photoinitiator-coating composition is placed underneath a layer
26 which is somewhat opaque to the radiation used, more initiator may be
27 needed. For most purposes, however, the amount of photoinitiator, when
28 used, will be in the range of 0.01 to 10% by weight of the total composition.
29 The initiating of oxygen scavenging can be accomplished by exposing the
30 packaging article to actinic or electron beam radiation, as described below.

1 Antioxidants may be incorporated into the scavenging compositions of this
2 invention to control degradation of the components during compounding and
3 shaping. An antioxidant, as defined herein, is any material which inhibits
4 oxidative degradation or cross-linking of polymers. Typically, such
5 antioxidants are added to facilitate the processing of polymeric materials
6 and/or prolong their useful shelf-life.

7 Antioxidants such as Vitamin E, Irganox® 1010, Irganox® 1076,
8 2,6-di(t-butyl)-4-methyl-phenol(BHT), 2,6-di(t-butyl)-4-ethyl-phenol (BHEB),
9 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite,
10 tris-(nonylphenyl)phosphite and dilaurylthiodipropionate would be suitable for
11 use with this invention.

12 When an antioxidant is included as part of the present composition, it should
13 be used in amounts which will prevent oxidation of the scavenger
14 composition's components as well as other materials present in a resultant
15 blend during formation and processing but the amount should be less than
16 that which would interfere with the scavenging activity of the resultant layer,
17 film or article. The particular amount needed will depend on the particular
18 components of the composition, the particular antioxidant used, the degree
19 and amount of thermal processing used to form the shaped article, and the
20 dosage and wavelength of radiation applied to initiate oxygen scavenging and
21 can be determined by conventional means. Typically, they are present in
22 about 0.01 to 1% by weight.

23 Other additives which may also be included in oxygen scavenger layers
24 include, but are not necessarily limited to, fillers, pigments, dyestuffs,
25 stabilizers, processing aids, plasticizers, fire retardants, anti-fog agents, etc.

26 The amounts of the components which are used in the oxygen scavenging
27 compositions, or layers have an effect on the use, effectiveness and results of
28 this method. Thus, the amounts of polymer, transition metal catalyst and any

1 photoinitiator, antioxidant, polymeric diluents and additives, can vary
2 depending on the article and its end use.

3 For instance, one of the primary functions of the polymer described above is
4 to react irreversibly with oxygen during the scavenging process, while the
5 primary function of the transition metal catalyst is to facilitate this process.
6 Thus, to a large extent, the amount of polymer present will affect the oxygen
7 scavenging capacity of the composition, i.e., affect the amount of oxygen that
8 the composition can consume. The amount of transition metal catalyst will
9 affect the rate at which oxygen is consumed. Because it primarily affects the
10 scavenging rate, the amount of transition metal catalyst may also affect the
11 onset of oxygen scavenging (induction period).

12 It has been found that the subject polymers, when used as part of the present
13 composition, provide oxygen scavenger properties at desirable rate and
14 capacity while causing the composition to have enhanced processability and
15 compatibility properties over conventional ethylenically unsaturated polymers.
16 Thus, the present composition can be used to provide, by itself or as a blend
17 with diluent polymers, such as polyolefins and the like, a packaging material
18 or film having enhanced processability properties. Further, the present
19 composition consumes and depletes the oxygen within a package cavity
20 without substantially detracting from the color, taste and/or odor of the product
21 contained within the package cavity.

22 The amount of the above-described polymer contained as part of the present
23 composition may range from about 1 to 100% by weight of the composition or
24 layer composed of said composition in which both polymer and transition
25 metal catalyst are present (hereinafter referred to as the "scavenging
26 composition", e.g., in a coextruded film or container, the scavenging
27 composition would comprise the particular layer(s) in which both the
28 copolymer and transition metal catalyst components are present together).
29 Typically, the amount of transition metal catalyst may range from 0.001 to 1%

1 (10 to 10,000 ppm) of the scavenging composition, based on the metal
2 content only (excluding ligands, counterions, etc.). In the event the amount of
3 transition metal catalyst is less than 1%, it follows that the polymer and any
4 additives will comprise substantially all of the remainder of the composition.
5 The polymer of the present invention may further be combined with other
6 polymeric oxygen scavenger agents.

7 Any further additives employed normally will not comprise more than 10% of
8 the scavenging composition, with preferable amounts being less than 5% by
9 weight of the scavenging composition.

10 Optionally, the compositions and process of this invention can include
11 exposure of the polymer containing the oxygen scavenging-promoting
12 transition metal to actinic radiation to reduce the induction period, if any,
13 before oxygen scavenging commences. A method is known for initiating
14 oxygen scavenging by exposing a film comprising an oxidizable organic
15 compound and a transition metal catalyst to actinic radiation. A composition
16 of the present invention which has a long induction period in the absence of
17 actinic radiation but a short or non-existent induction period after exposure to
18 actinic radiation is particularly preferred. They maintain a high capability for
19 scavenging oxygen upon activation with actinic radiation. Thus, oxygen
20 scavenging can be activated when desired.

21 The radiation used in this method should be actinic, e.g., ultraviolet or visible
22 light having a wavelength of about 200 to 750 nanometers (nm), and
23 preferably having a wavelength of about 200 to 600 nm, and most preferably
24 from about 200 to 400 nm. When employing this method, it is preferable to
25 expose the oxygen scavenger to at least 0.01 Joule per gram of scavenging
26 composition. A typical amount of exposure is in the range of 10 to
27 2000 Joules per gram. The radiation can also be an electron beam radiation
28 at a dosage of about 2 to 200 kiloGray, preferably about 10 to 100 kiloGray.
29 Other sources of radiation include ionizing radiation such as gamma, X-rays

1 and corona discharge. The duration of exposure depends on several factors
2 including, but not limited to, the amount and type of photoinitiator present,
3 thickness of the layers to be exposed, thickness and opacity of intervening
4 layers amount of any antioxidant present, and the wavelength and intensity of
5 the radiation source. The radiation provided by heating of polyolefin and the
6 like polymers (e.g., 100-250°C) during processing does not cause triggering.

7 Oxygen-scavenging compositions of the present invention are useful in many
8 ways. The compositions can be dispersed as small particles for absorbing
9 oxygen or can be coated onto materials such as metallic foil, polymer film,
10 metalized film, paper or cardboard to provide, in some embodiments,
11 scavenging properties and/or adhesive properties. The compositions are also
12 useful in making articles such as single or multi-layer rigid thick-walled plastic
13 containers or bottles (typically, between 5 and 100 mils in thickness) or in
14 making single or multi-layer flexible films, especially thin films (less than
15 5 mils, or even as thin as about 0.25 mil). Some of the compositions of the
16 present invention are easily formed into films using well-known means. These
17 films can be used alone or in combination with other films or materials.

18 The compositions of the present invention may be further combined with one
19 or more polymers, such as thermoplastic polymers which are typically used to
20 form film layers in plastic packaging articles. In the manufacture of certain
21 packaging articles, well-known thermosets can also be used as a polymeric
22 diluent.

23 Selecting combinations of a diluent and the composition of the present
24 invention depends on the properties desired. Polymers which can be used as
25 the diluent include, but are not limited to, polyethylene, low or very low density
26 polyethylene, polypropylene, polyvinyl chloride, and ethylene copolymers
27 such as ethylene-vinyl acetate, ethylene-alkyl acrylates or methacrylates,
28 ethylene-acrylic acid or methacrylic acid, and ethylene-arylic or metharylic
29 acid ionomers. In rigid packaging applications, polystyrene is often used.

1 Blends of different diluents may also be used. However, as indicated above,
2 the selection of the polymeric diluent largely depends on the article to be
3 manufactured and the end use. Such selection factors are well known in the
4 art.

5 If a diluent polymer such as a thermoplastic is employed, it should further be
6 selected according to its compatibility with the composition of the present
7 invention. In some instances, the clarity, cleanliness, effectiveness as an
8 oxygen-scavenger, barrier properties, mechanical properties and/or texture of
9 the article can be adversely affected by a blend containing a polymer which is
10 incompatible with the composition of the present invention.

11 A blend of a composition of the present invention with a compatible polymer
12 can be made by dry blending or by melt-blending the polymers together at a
13 temperature in the approximate range of 50°C to 250°C. Alternative methods
14 of blending include the use of a solvent followed by evaporation. When
15 making film layers or articles from oxygen-scavenging compositions, extrusion
16 or coextrusion, solvent casting, injection molding, stretch blow molding,
17 orientation, thermoforming, extrusion coating, coating and curing, lamination
18 or combinations thereof would typically follow the blending.

19 Layers comprising the composition of the present invention may be in several
20 forms. They may be in the form of stock films, including "oriented" or "heat
21 shrinkable" films, which may ultimately be processed as bags, etc., or in the
22 form of stretch-wrap films. The layers may also be in the form of sheet inserts
23 to be placed in a packaging cavity. In rigid articles such as beverage
24 containers, thermoformed trays or cups, the layer may be within the
25 container's walls. Even further, the layer may also be in the form of a liner
26 placed with or in the container's lid or cap. The layer may even be coated or
27 laminated onto any one of the articles mentioned above.

1 In multi-layered articles, the scavenging layer comprising the composition of
2 the present invention may be included with layers such as, but not necessarily
3 limited to, "oxygen barriers", i.e., layers of material having an oxygen
4 transmission rate equal to or less than 100 cubic centimeters-mil per square
5 meter (cc-mil/m²) per day per atmosphere pressure at room temperature, i.e.,
6 about 25°C. Typical oxygen barriers comprise poly(ethylene vinyl alcohol),
7 polyacrylonitrile, polyvinyl chloride, poly(vinylidene dichloride), polyethylene
8 terephthalate, silica and polyamides. Metal foil layers can also be employed.

9 Other additional layers may include one or more layers which are permeable
10 to oxygen. In one preferred packaging construction, especially for flexible
11 packaging for food, the layers include, in order starting from the outside of the
12 package to the innermost layer of the package, (i) an oxygen barrier layer,
13 (ii) a scavenging layer, i.e., the scavenging composition as defined earlier,
14 and, optionally, (iii) an oxygen permeable layer. Control of the oxygen barrier
15 property of (i) allows a means to regulate the scavenging life of the package
16 by limiting the rate of oxygen entry to the scavenging composition (ii), and
17 thus limiting the rate of consumption of scavenging capacity. Control of the
18 oxygen permeability of layer (iii) allows a means to set an upper limit on the
19 rate of oxygen scavenging for the overall structure independent of the
20 composition of the scavenging composition (ii). This can serve the purpose of
21 extending the handling lifetime of the films in the presence of air prior to
22 sealing of the package. Furthermore, layer (iii) can provide a barrier to
23 migration of the individual components in the scavenging films or by-products
24 of scavenging into the package interior. Even further, layer (iii) also improves
25 the heat-sealability, clarity and/or resistance to blocking of the multi-layer film.

26 Further, additional layers such as adhesive layers may also be used.
27 Compositions typically used for adhesive layers include anhydride functional
28 polyolefins and other well-known adhesive layers.

1 To determine the oxygen scavenging capabilities of a composition, the rate of
2 oxygen scavenging can be calculated by measuring the time that elapsed
3 before the article depletes a certain amount of oxygen from a sealed
4 container. For instance, a film comprising the scavenging component can be
5 placed in an air-tight, sealed container of a certain oxygen containing
6 atmosphere, e.g., air which typically contains 20.9% oxygen by volume.
7 Then, over a period of time, samples of the atmosphere inside the container
8 are removed to determine the percentage of oxygen remaining. The
9 scavenging rates of the composition and layers of the present invention will
10 change with changing temperature and atmospheric conditions.

11 When an active oxygen barrier is prepared, the scavenging rate can be as low
12 as 0.1 cc oxygen per gram of composition of the present invention per day in
13 air at 25°C and a 1 atmosphere pressure. However, preferable compositions
14 of this invention have rates equal to or greater than 1 cc oxygen per gram per
15 day, thus making them suitable for scavenging oxygen from within a package,
16 as well as suitable for active oxygen barrier applications. Many compositions
17 are even capable of more preferable rates equal to or greater than 5.0 cc O₂
18 per gram per day.

19 Generally, film layers suitable for use as an active oxygen barrier can have an
20 oxygen transmission rate as high as 10 cc oxygen per square meter per mil
21 per day when measured in air at 25°C and 1 atmosphere pressure.
22 Preferably, a layer of this invention has an oxygen transmission rate less than
23 about 1 cc oxygen per square meter per mil per day, and more preferably has
24 an oxygen transmission rate less than about 0.2 cc oxygen per square meter
25 per rail per day under the same conditions, thus making it suitable for active
26 oxygen barrier applications as well as for scavenging oxygen from within a
27 package.

28 In an active oxygen barrier application, it is preferable that the combination of
29 oxygen barriers and any oxygen scavenging activity create an overall oxygen

1 transmission rate of less than about 1.0 cubic centimeter-mil per square meter
2 per day per atmosphere pressure at 25°C. Another definition of acceptable
3 oxygen scavenging is derived from testing actual packages. In actual use, the
4 scavenging rate requirement will largely depend on the internal atmosphere of
5 the package, the contents of the package and the temperature at which it is
6 stored.

7 In a packaging article made according to this invention, the scavenging rate
8 will depend primarily on the amount and nature of the composition of the
9 present invention in the article, and secondarily on the amount and nature of
10 other additives (e.g., diluent polymer, antioxidant, etc.) which are present in
11 the scavenging component, as well as the overall manner in which the
12 package is fabricated, e.g., surface area/volume ratio.

13 The oxygen scavenging capacity of an article comprising the invention can be
14 measured by determining the amount of oxygen consumed until the article
15 becomes ineffective as a scavenger. The scavenging capacity of the package
16 will depend primarily on the amount and nature of the scavenging moieties
17 present in the article, as discussed above.

18 In actual use, the oxygen scavenging capacity requirement of the article will
19 largely depend on three parameters of each application:

- 20 (1) the quantity of oxygen initially present in the package;
- 21 (2) the rate of oxygen entry into the package in the absence of the
22 scavenging property; and
- 23 (3) the intended shelf life for the package.

24 The scavenging capacity of the composition can be as low as 1 cc oxygen per
25 gram, but is preferably at least 10 cc oxygen per gram, and more preferably at

1 least 50 cc oxygen per gram. When such compositions are in a layer, the
2 layer will preferably have an oxygen capacity of at least 250 cc oxygen per
3 square meter per mil thickness and more preferably at least 500 cc oxygen
4 per square meter per mil thickness.

5 Other factors may also affect oxygen scavenging and should be considered
6 when selecting compositions. These factors include but are not limited to
7 temperature, relative humidity, and the atmospheric environment in the
8 package.

9 Non-limiting examples are given in Examples 1 and 2 below of experimental
10 conditions that were used for preparation of the polymers. Non-limiting
11 examples of the resin preparation followed by steam stripping as well as
12 compounding the polymers with oxidation catalyst, such as cobalt oleate and
13 a photoinitiator, such as Methanone, [5'-(5'-(4-benzoylphenyl)[1,1':3',
14 1"-terphenyl]-4,4"-diyl]bis[phenyl- (hereinafter referred to as BBP³), and
15 extruded into a 3-layer film having a PE/oxygen scavenging polymer/PE
16 structure are provided in Examples 3 through 6 below.

17 Headspace studies of three layer films made by compounding catalyst
18 package with both fresh and aged (20 months stored in air at ambient
19 temperature) resins after UV triggering give a very fast rate of oxygen
20 scavenging and the resulting packages are relatively non-odorous.

21 Non-limiting examples of such studies are given in Examples 7 and 8.

22 Furthermore, the above polymer can be further diluted by a lower cost oxygen
23 permeable resin, such as EBAC or PE or EVA, down to 50 and even 25% of
24 the original concentration and still maintain a high oxygen scavenging rate, as
25 the non-limiting examples in Examples 9 and 10 show.

EXAMPLES

Example 1

Polymer Preparation (C1641-6)

550 ml of decalin® was placed in a flask. To this was added 350 g of Chevron EMAC SP-2260 which has 24 weight % of methyl acrylate (0.9767 moles of methyl acrylate) and 0.48 g of Irganox®1076 (0.1 mole). The temperature of the mixture was gradually raised while stirring. When the temperature reached approximately 120°C, 127.1 g (0.9767 moles) of 3-methyl-cyclohex-1-ene-4-methanol (97%) was added. When the temperature reached approximately 140°C, 4.8 g of the catalyst $\text{Ti}(\text{OC}_2\text{H}_5)_4$ was added a portion at a time. The temperature was maintained at 170°C while stirring. The course of the reaction was observed by subjecting samples of the mixture to NMR at hourly intervals. The percent conversion is given in Table 1 below. After 5 hours of reaction, the mixture was cooled and 400 ml of CHCl_3 was added and the mixture was then precipitated by adding it to 4 liters of CH_3OH in a Waring blender. The precipitate is filtered and washed with CH_3OH and dried in a vacuum oven at 50°C. The dried mixture yielded 407.5 g of ethylene/methyl acrylate/methyl cyclohexene methyl acrylate (EMCM).

Table 1

Time (hours)	Percent Conversion
1 hour	50%
2 hours	62.3%
3 hours	65.5%
5 hours	87.1%

390 grams of a combination of the above prepared polymer and the same polymer prepared under the same conditions in a different batch, which

1 together have a conversion percentage of 68.8%, was solvent coated with
2 3.25 g cobalt-neodecanoate in 70 ml normal hexane. The mixture was tumble
3 dried for 1.5 hours and residual solvent removed in a vacuum.

4 Example 2

5 Polymer Preparation

6 600 ml of decalin was placed in a flask. To this was added 334 grams of
7 Chevron SP-2260 (0.9330 moles of methyl acrylate) and 0.44 g of Irganox®
8 1010 (0.1% mole). The temperature of the mixture was gradually raised while
9 stirring. When the temperature reached approximately 120°C, 104.6 g
10 (0.93 moles) of cyclohex-1-ene-4-methanol was added. When the
11 temperature reached approximately 140°C, 4.4 g of the catalyst $\text{Ti}(\text{OC}_2\text{H}_5)_4$
12 was added a portion at a time. The temperature was maintained at 160°C
13 while stirring. The course of the reaction was observed by subjecting samples
14 of the mixture to NMR at hourly intervals. The percent conversion is given in
15 Table 2 below. After 3 hours of reaction, the mixture was cooled and 400 ml
16 of CHCl_3 was added and the mixture was then precipitated by adding it to
17 4 liters of CH_3OH in a Waring blender. The precipitate was filtered and
18 washed with CH_3OH and dried in a vacuum oven at 50°C. The dried mixture
19 yielded 380.5 g of polymer.

20 Table 2

Time (hours)	Percent Conversion
1 hour	43.8%
2 hours	56.7%
3 hours	55.7%

21
22 185 grams of the above-prepared polymer was combined with 45 ml normal
23 hexane and 1.54 g cobalt-neodecanoate resulting in 1000 ppm of cobalt ion
24 and 0.0185 g Irganox® 1010 resulting in 100 ppm Irganox®. The mixture was

1 heated and blended and then dried in a vacuum-oven. The resulting
2 compound was extruded into a film.

3 Additionally, 185 grams of the above-prepared polymer was combined with
4 45 ml normal hexane and 1.54 g cobalt-neodecanoate (resulting in 1000 ppm
5 of cobalt ion) and 0.046 g Irganox® 1010 (resulting in 250 ppm Irganox®).
6 The mixture is heated and blended and then dried in a vacuum-oven. The
7 resulting compound is extruded into a film.

8 Example 3

9 EMCM Made in ZSK-30 Extruder

10 Ethylene-methyl acrylate copolymer (EMAC) was fed into a Werner &
11 Pfleiderer ZSK-30 twin screw extruder at 6 kg/hr, and the reactants and
12 catalysts were added to the extruder in a subsequent reaction zone. The
13 catalyst $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was added with the reactants at 3 mol % or at a rate of
14 148 cc/hr. Irganox®/Toluene solution was added at 4.5 g/900 cc using a
15 Milton Roy 29/290 mini-pump. To obtain 100 ppm of Irganox®, it must be
16 added at 2.2 cc/min. To obtain 50 ppm of Irganox, it must be added at
17 1.1 cc/min. Cyclohexane methyl alcohol with 1,000 ppm of an antioxidant of
18 BHT was added via a Milton Roy dual head at 1958 cc/hr. Steam is injected
19 into the system at 800 cc $\text{H}_2\text{O}/\text{Hr}$ at the end of the reaction zone.

20 51 lbs of EMCM product (100 ppm Irganox® 1010, 59.3% methyl alcohol
21 (MA), 2.98 g/10 min. Melt Flow) was produced over a period of approximately
22 2 hours.

1

Example 4

2

EMCM Made in ZSK-30

3 45 lbs of EMCM product (100 ppm Irganox®1010, 2.38 g/10 min Melt Index)
4 was extruded over a period of approximately 3 hours. A dual steam stripping
5 setup was used in which pressurized injectors at zones 4 and 11 of the
6 extruder pumped steam at 1076 cc/hr and 728 cc/hr, respectively. Both
7 injectors were Pulse 680 pumps with a pressure of at least 800 psi, except at
8 the first measured time interval when injector (No. 4) was measured at
9 500-550 psi and injector (No. 11) was measured at 500 psi.

10

Example 5

11 Co-polymerization of Styrene and 3-Cyclohexene-1-Methanol Methacrylate

12 In a 1-liter round bottom flask, 65 grams styrene (0.625 mole), 113 grams of
13 3-cyclohexene-1-methanol methacrylate (0.625 mole), 1.25 grams of Benzoyl
14 peroxide and 450 grams of toluene were mixed and degassed by freeze-thaw
15 cycles. The degassed solution was polymerized at 70-75°C for 48 hours and
16 discharged into 2 liters of methanol in a Waring Blender. The product isolated
17 was dried in a vacuum oven at 50°C for 2 hours to give 155 grams of
18 co-polymer. NMR analysis indicates it contains 48 mole % of styrene and
19 52 mole % of 3-cyclohexene-1-methanol methacrylate. Tg by DSC is 66°C.

20

Example 6

21

Oxygen Scavenging Test of Styrene/CHMA Copolymer

22 90 weight % of the above-mentioned co-polymer and 10 weight % of a EVA
23 based Master batch containing 1 weight % of co-oleate and 1 weight % of a
24 photoinitiator (BBP³) were processed into a 8 mil thick monolayer film. A
25 100 cm² film was irradiated at both sides to receive 800 mJoules/cm² of
26 254 nm UV on each side and sealed into a foil bag containing 300 cc of 1%

1 oxygen. The oxygen uptake was monitored up to 11 days at 4°C and at room
2 temperature. The results are shown in Tables 3 (4°C) and 4 (room
3 temperature).

4 Table 3

Time (days)	O ₂ Meas. Vol%	O ₂ Meas. Vol, ml	Vol—O ₂ Used ml	O ₂ Uptake ml/g	O ₂ Uptake Avg Rate cc/m ² /day	Instant Rate cc/m ² /day	O ₂ Capacity cc/m ² /mil
0.0	1.05	3.15	0.00	0.00	0.00	0.00	0.00
1.1	0.94	2.77	0.32	0.18	14.79	14.79	1.62
3.9	0.49	1.42	1.63	0.92	20.73	23.03	8.15
4.8	0.39	1.11	1.91	1.08	19.81	15.78	9.57
7.0	0.30	0.84	2.17	1.22	15.40	5.72	10.83
11.0	0.09	0.25	2.74	1.54	12.43	7.22	13.72

6 Table 4

Time (days)	O ₂ Meas. Vol%	O ₂ Meas. Vol, ml	Vol—O ₂ Used ml	O ₂ Uptake ml/g	O ₂ Uptake Avg Rate cc/m ² /day	Instant Rate cc/m ² /day	O ₂ Capacity cc/m ² /mil
0.0	1.04	3.12	0.00	0.00	0.00	0.00	0.00
1.1	0.48	1.42	1.65	1.03	75.28	75.28	8.26
3.9	0.09	0.26	2.78	1.73	35.40	19.96	13.92
4.8	0.04	0.11	2.93	1.82	30.26	7.89	14.63
7.0	0.01	0.03	3.01	1.87	21.39	1.91	15.05
11.0	0.01	0.03	3.01	1.87	13.64	0.00	15.05

8 Example 7

9 Polymerization of 3-cyclohexene-1-methanol acrylate

10 75 grams (0.45 mole) of 3-cyclohexene-1-methanol acrylate (CHAA), 200 ml
11 of toluene and 0.5 grams of Benzoyl peroxide were charged into a 500 ml
12 round-bottomed flask and degassed by freeze-thaw cycles. The degassed

5

6

7

8

20 capacity is based on the total weight of the three-layer film.

1

Table 5

Time (days)	O ₂ Meas. Vol%	O ₂ Meas. Vol, ml	Vol—O ₂ Used ml	O ₂ Uptake ml/g	O ₂ Uptake Avg Rate cc/m ² /day	Instant Rate cc/m ² /day	O ₂ Capacity cc/m ² /mil
0.0	1.04	3.12	0.00	0.00	0.00	0.00	0.00
0.8	0.74	2.18	0.89	1.84	57.93	57.93	44.25
1.9	0.46	1.33	1.70	3.54	45.85	37.36	84.85
3.0	0.29	0.83	2.18	4.54	36.87	21.87	109.08
5.8	0.14	0.39	2.60	5.42	22.46	7.41	130.08
7.8	0.09	0.25	2.74	5.71	17.67	3.51	136.95

2

3

Example 9

4

Headspace Analysis of O₂ Scavenging in

5

Dowlex® 3010/EMCM/Dowlex® 3010 Films

6 Oxygen scavenging analysis was performed using a Mocon HS750 with a
7 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
8 film with Dowlex® 3010 film for the two outside layers and steam stripped
9 EMCM for the middle layer (50 ppm Irganox 1010)). The thickness of the
10 layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle
11 layer comprised 1000 ppm Cobalt salt, 1000 ppm BBP³ (a photoinitiator)
12 exposed for 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The
13 oxygen scavenging was tested with 300 cc 1% O₂ at 4°C. These results are
14 plotted along with the results of Example 7 in Figure 2, which graphically plots
15 % oxygen in headspace against time (days).

Example 10

Headspace Analysis of O₂ Scavenging in Dowlex® 3010/
EBAC:EMCM/Dowlex® 3010 Films

Oxygen scavenging analysis was performed using a Mocon HS750 with a headspace volume of 300 cc. The sample tested was a 0.45 g three-layer film with Dowlex® 3010 film for the two outside layers and 3:1 EBAC (ethylene/butyl acrylate copolymer):EMCM (ethylene/methyl acrylate/cyclohexenyl methyl acrylate) for the middle layer (50 ppm Irganox® 1010)). The thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer comprised 1000 ppm of Cobalt salt, 1000 ppm BBP³ was exposed for 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen scavenging was tested with 300 cc 1% O₂ at 4°C. These results are plotted along with the results of Example 8 in Figure 3, which graphically plots % oxygen in headspace against time (days).

Example 11

Headspace Analysis of O₂ Scavenging in Dowlex® 3010/
EBAC:EMCM/Dowlex® 3010 Films

Oxygen scavenging analysis was performed using a Mocon HS750 with a headspace volume of 300 cc. The sample tested was a 0.47 g three-layer film with Dowlex® 3010 film for the two outside layers and 1:1 EBAC:EMCM for the middle layer (50 ppm Irganox®1010)). The thickness of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP³ exposed for 1.6 minutes at 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen scavenging was tested with 300 cc 1% O₂ at 4°C. The results of the tests are given below in Table 6. These results are plotted along with the results of Example 9 in Figure 3, which graphically plots % oxygen in headspace

1 against time (days). The oxygen scavenging uptake capacity is based on the
2 total weight of the 3-layer film.

3 Table 6

Time (days)	Head-space O ₂ (Vol%)	Head-space O ₂ (Vol, ml)	Vol—O ₂ Used (ml)	O ₂ Uptake (ml/g)	O ₂ Uptake Avg Rate (cc/m ² ·day)	Instant Rate (cc/m ² ·day)	O ₂ Capacity cc/m ²
0.0	1.09	3.27	0.00	0.00	0.00	0.00	0.00
0.8	0.74	2.18	1.03	2.20	63.00	63.00	51.63
1.8	0.50	1.45	1.73	3.68	48.52	36.18	86.43
4.8	0.17	0.48	2.67	5.8	27.73	15.51	133.45
6.1	0.12	0.34	2.81	5.98	23.17	5.60	140.45
6.9	0.10	0.28	2.86	6.09	20.84	3.40	143.20
7.9	0.08	0.22	2.92	6.21	18.46	2.62	145.90

4
5 Example 12

6 Headspace Analysis of O₂ Scavenging Capacity
7 in Dowlex® 3010/EMCM/Dowlex® 3010 Films

8 Oxygen scavenging analysis was performed using a Mocon HS750 with a
9 headspace volume of 300 cc. The sample tested was a 0.47 g three-layer
10 film with Dowlex® 3010 film for the two outside layers and steam stripped
11 EMCM for the middle layer (50 ppm Irganox®1010)). The thickness of the
12 layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle
13 layer comprised 1000 ppm Cobalt Oleate salt, 1000 ppm BBP³ exposed for
14 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen
15 scavenging was tested with 300 cc air at room temperature. The O₂ uptake
16 capacity is based on total weight of the 3-layer film. The results of the tests
17 are given below in Table 7. These results are plotted along with the results of
18 Example 12 in Figure 4, which graphically plots % oxygen in headspace
19 against time (days).

Table 7

Time (days)	Head-space O ₂ (Vol%)	O ₂ Vol, (ml)	Vol-O ₂ Used (ml)	O ₂ Uptake (ml/g)	O ₂ Uptake Avg Rate (cc/m ² ·day)	Instant Rate (cc/m ² ·day)	O ₂ Capacity (cc/m ²)
0.0	20.60	61.80	0.00	0.00	0.0	0.0	0.0
1.0	13.40	39.53	21.24	43.35	1058	1058	1062
2.0	12.20	35.38	24.72	50.45	616	173	1236
3.0	11.80	33.63	25.86	52.78	437	60	1293
6.2	11.80	33.04	25.86	52.78	207	0.0	1293

Example 13

Headspace Analysis of O₂ Scavenging Capacity in Dowlex® 3010/EBAC:EMCM/Dowlex® 3010 Films

Oxygen scavenging analysis was performed using a Mocon HS750 with a headspace volume of 300 cc. The sample tested was a 0.45 g three-layer film with Dowlex® 3010 film for the two outside layers and 2:1 EBAC:EMCM for the middle layer (50 ppm Irganox 1010)). The width of the layers was 0.5/1/0.5 +/- 0.1 Mil. The oxygen scavenging portion of the middle layer comprised 1000 ppm of Cobalt salts, 1000 ppm BBP³ exposed for 1.6 minutes to 254 nm UV at 1 inch to receive 800 mJ/cm². The oxygen scavenging was tested with 300 cc air at room temperature. The O₂ uptake capacity is based on total weight of the 3-layer film. The results of the tests are given below in Table 8. These results are plotted along with the results of Example 9 in Figure 4, which graphically plots % oxygen in headspace against time (days).

Table 8

Time (days)	Head-space O ₂ (Vol%)	Head-space O ₂ Vol, (ml)	Vol-O ₂ Used (ml)	O ₂ Uptake (ml/g)	O ₂ Uptake Avg Rate (cc/m ² ·day)	Instant Rate (cc/m ² ·day)	O ₂ Capacity (cc/m ²)
0.0	20.60	61.80	0.00	0.00	0.0	0.0	0.0
1.0	17.70	52.21	8.56	18.20	426	426	428
2.0	17.40	50.46	9.43	20.05	235	43	471
3.0	17.10	48.74	10.28	21.87	174	45	514
6.2	17.10	47.88	10.28	21.87	83	0.0	514

Example 14

Taste Preference Test

The organoleptic quality of a film containing EMCM as the scavenging resin in a multi-layer oxygen scavenging packaging structure was evaluated and compared with an SBS (styrene/butadiene/styrene)-based oxygen scavenging packaging structure. Films were triggered with 800 mJ/cm² of 254 nm UV. Packages containing ca. 200 ml of water were made and vacuum/gas flushed to obtain a gas composition of 1% O₂:99% N₂. Packages were stored at 40°F for seven days prior to taste testing. A forced preference double blind Triangle taste test was carried out on water extracts of the EMCM-based and SBS-based films.

Sensory results indicated that there was a significant difference (24 out of 28 respondents) between the EMCM-based and SBS-based structures. All 24 respondents who correctly identified the odd sample in the single test preferred the taste of the water packaged in EMCM over SBS. As shown in Table 9, Day 4 scavenging rates of the EMCM-based structures were lower than the SBS counterpart. On Day 4, both structures had significant oxidation and the obvious difference in flavor perception was attributed to the fewer and

1 less objectionable by-products (fragments after oxidation of EMCM) of the
2 EMCM oxygen scavenging system.

3 In a second forced preference triangle taste test, water samples in
4 EMCM-based scavenging structures were tested against water samples
5 packaged in a standard barrier laminate film (R660B manufactured by
6 Cryovac Division of Sealed Air Corporation). The packaged water extract
7 samples were submitted to a sensory panel for forced preference double blind
8 taste testing. Samples were tested after 8 days of scavenging. A significant
9 difference in the taste was found between the samples packaged in the
10 EMCM and the control packages. Surprisingly, the preference was towards
11 the EMCM structure. Open comments stated that there was no off-flavor
12 (normally associated with the SBS-based oxygen scavenging films) in the
13 EMCM samples and that EMCM was "pretty close in taste to the control."
14 Headspace oxygen levels reached by the EMCM structure were ca. 0.2%
15 (down from 1%) at Day 8. Scavenging results of the EMCM film used during
16 this test are also listed in Table 9.

17 Table 9
18 Oxygen Scavenging
19 Packaging Films

Film Sample	Average Rate (cc/m ² ·day)	Average Rate (cc/m ² ·day)	Induction Period (days)	Peak Instantaneous Rate avg. (c) (cc/m ² ·day)	Peak Instantaneous Rate (cc/m ² ·day)
	Mean	St. dev.		Mean	St. dev.
SBS Film	51.0 ^a	7.8	<1	88.4 (1)	14.1
1 st Sensory test EMCM	41.6 ^a	5.3	<1	68.6 (2)	11.4
2 nd Sensory Test EMCM	30.5 ^b	5.9	<1	83.6 (2-3)	19.4

20 ^aRate at 4 days.

21 ^bRate at 8 days.

22 ^cTime to reach peak rate in days.

Example 15

Taste Preference Test

Oxygen scavenging test films, 5 cm x 20 cm, were irradiated with 800 mJ/cm² ultraviolet (254 nm) and heat tacked to the top of the test pouches (one per pouch). The pouches (16 cm x 19 cm) were made from laminated barrier film specifically designed to be oxygen impermeable. 21 gram slices of freshly sliced turkey roll were put into sterilized 9 cm petri dishes (one per dish). The dishes were, in turn, placed into the barrier pouches (one per pouch). The pouches were heat sealed, filled with 300 cc 1% oxygen/99% nitrogen gas, and stored at 4°C for the duration of the test.

Two types of oxygen scavenging polymers were compared in the test against a control (barrier pouch alone, no oxygen scavenger). The oxygen scavenging films were each three layer (ABA) structures in which the outer, "A", layer was 0.5 mil thick LLDPE, and the middle, "B", layer was 1.0 mil thick oxygen scavenging polymer (compounded with 1000 ppm cobalt (as oleate) and 1000 ppm of a photoinitiator (BBP³). The headspace oxygen for the pouches is shown in Table 10. Both of the test oxygen scavenging films scavenged more oxygen than the packaged turkey itself.

Table 10

Oxygen scavenging layer composition	Initial headspace oxygen, %	Headspace oxygen after 3 days @ 4°C, %
none	1.02	0.72
SBS	1.00	0.08
EMCM	1.02	0.17

Taste panelists were instructed to force rank the samples according to their taste preference; assigning the least preferred sample a score of 1, and the most preferred sample a score of 10. As is shown in Figure 5, the panelists

1 found the taste of the turkey packaged in control and the EMCM pouches
2 statistically equivalent. The turkey packaged in the SBS pouch was found
3 significantly less preferred than either the control or the EMCM.

4 Example 16

5 Polymerization of EMCM via high pressure autoclave reactor proceeds in a
6 steady-state continuous manner as follows. Ethylene is circulated at a rate of
7 10,000-14,000 lb/hr by a hypercompressor which compresses the ethylene to
8 16,500-22,500 psig. The compressed ethylene is injected into the autoclave
9 reactor in various positions along the reactor wall associated with the zone
10 divisions made by the reactor internals. Simultaneously, acrylate of
11 cyclohexene-1-methanol (CHAA) comonomer is injected into either the first
12 zone or the first and second zones of the reactor at a rate sufficient to
13 produce a copolymer containing from 5 to 40% CHAA, more typically
14 10%-25% by weight. The reaction is initiated by injection of a solution of
15 di-tert butyl peroxyvalate in an aliphatic solvent which also functions as a
16 chain transfer agent. The initiator is injected at a rate to provide
17 approximately 10-20 ppm (wt) of initiator in the compressed ethylene.

18 The locations of the CHAA injection are critical to the polymer being
19 produced, as is shown in U.S. Patent No. 5,571,878 which details the effects
20 of acrylate injection location on the polymerization of ethylene and an alkyl
21 acrylate comonomer in a high pressure system.

22 The resultant polymer exits the reactor at a rate of 1000-2000 lb/hr in a
23 multi-phase solution in ethylene to a high pressure separator. The pressure
24 of the product is reduced adiabatically through a valve to 2,000 psig pressure
25 and the unreacted ethylene and unreacted CHAA are recompressed to
26 reactor pressure and reinjected into the reactor for further polymerization.
27 Additional ethylene is added to the cycle via a primary compressor which

1 compresses the ethylene from pipeline pressure to the suction pressure of the
2 hypercompressor at a rate equal to the polymer production rate.

3 From the high pressure separator, the polymer is reduced in pressure to
4 4-10 psig for further removal of unreacted ethylene and unreacted
5 comonomer. The polymer is fed into a melt pumping device (either an
6 extruder or a gear pump) and is pelletized and transferred for packaging and
7 shipment.

8 Although a few embodiments of the invention have been described in detail
9 above, it will be appreciated by those skilled in the art that various
10 modifications and alterations can be made to the particular embodiments
11 shown without materially departing from the novel teachings and advantages
12 of the invention. Accordingly, it is to be understood that all such modifications
13 and alterations are included within the spirit and scope of the invention as
14 defined by the following claims.

1 WHAT IS CLAIMED IS:

2 1. A composition comprising a polymeric backbone, cyclic olefinic pendent
3 groups and linking groups linking the olefinic pendent groups to the
4 polymeric backbone.

5 2. A composition according to claim 1, wherein the polymeric backbone is
6 ethylenic and the linking groups are selected from the group consisting
7 of:

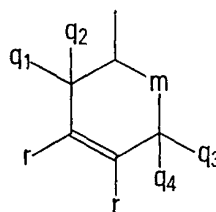
8 $-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;

9 $-(C=O)-NH-(CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

10 wherein R is hydrogen or an alkyl group selected from the group
11 consisting of methyl, ethyl, propyl and butyl groups and where n is an
12 integer in the range from 1 to 12.

13 3. The composition of claim 1, wherein the cyclic olefinic pendent groups
14 have the structure (I):

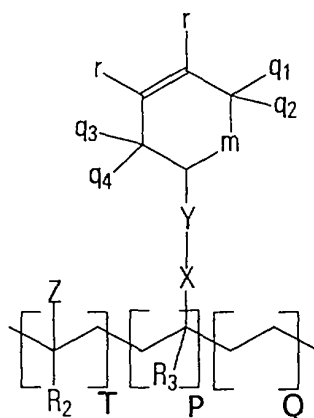
15 (I)



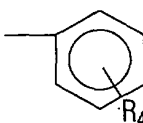
18 where q1, q2, q3, q4, and r are selected from the group consisting of -H, -
19 CH3, and -C2H5; and where m is $-(CH_2)_n-$ with n being an integer in the
20 range from 0 to 4; and wherein, when r is -H, at least one of q1, q2, q3
21 and q4 is -H.

- 1 4. The composition of claim 1, wherein the polymeric backbone comprises
2 monomers selected from the group consisting of ethylene and styrene.
- 3 5. The composition of claim 1, wherein the cyclic olefinic pendent groups
4 are grafted onto the linking groups of the polymeric backbone by an
5 esterification, transesterification, amidation or transamidation reaction.
- 6 6. The composition of claim 5, wherein the esterification, transesterification,
7 amidation or transamidation reaction is a solution reaction or a reactive
8 extrusion.
- 9 7. The composition of claim 5, wherein the esterification, transesterification,
10 amidation or transamidation reaction is catalyzed by a catalyst selected
11 from the group consisting of strong non-oxidizing acids, tertiary amines,
12 Group I alkoxides, Group IVB alkoxides, and Group IVA organometallics.
- 13 8. The composition of claim 7, wherein the catalyst is selected from a
14 group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl
15 titanate, tetraisopropyl titanate, tetra-n-propyl-titanate, tetraethyl titanate,
16 2-hydroxy-pyridine and dibutyltin dilaurate.
- 17 9. The composition of claim 1, wherein the polymeric backbone, linking
18 groups and cyclic olefin pendent groups comprise repeating units, each
19 unit having a structure (II) as follows:

(II)



wherein $P+T+Q$ is 100 mol % of the total composition; P is greater than 0 mol % of the total composition; Z is selected from the group consisting of an aryl group; $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group:



where R_4 is selected from the group consisting of $-CH_3$, $-C_2H_5$, and $-H$; R_1 is selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$ and $-C_4H_9$; R_2 and R_3 are selected from the group consisting of $-H$ and $-CH_3$; X is selected from the group consisting of $-O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$, $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell-$; ℓ is an integer in the range from 1 to 6; Y is $-(CHR)_n-$, where n is an integer in the range from 0 to 12, R being selected from the group consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an

1 integer in the range from 0 to 4; and wherein when r is -H, at least one
2 of q₁, q₂, q₃ and q₄ is -H.

3 10. The composition of claim 9, wherein the cyclic olefinic pendent groups
4 are selected from the group consisting of cyclohexene-4-methylene
5 radical, 1-methyl cyclohexene-4-methylene radical, 2-methyl
6 cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-methylene
7 radical, 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl
8 cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-
9 methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical,
10 cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene
11 radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl cyclohexene-
12 4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical, 1,5-
13 dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-
14 ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical,
15 cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
16 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl
17 cyclohexene-4-propylene radical, 1,2-dimethyl cyclohexene-4-propylene
18 radical, 1,5-dimethyl cyclohexene-4-propylene radical, 2,5-dimethyl
19 cyclohexene-4-propylene radical, 1,2,5-trimethyl cyclohexene-4-
20 propylene radical, cyclopentene-4-methylene radical, 1-methyl
21 cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-methylene
22 radical, 1,2-dimethyl cyclopentene-4-methylene radical, 3,5-dimethyl
23 cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
24 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical, 1,2,3-
25 trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
26 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-
27 methyl cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-
28 ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-
29 dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl cyclopentene-4-
30 ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene radical, 1,2,3-
31 trimethyl cyclopentene-4-ethylene radical, 1,2,3,5-tetramethyl

1 cyclopentene-4-ethylene radical, cyclopentene-4-propylene radical, 1-
2 methyl cyclopentene-4-propylene radical, 3-methyl cyclopentene-4-
3 propylene radical, 1,2-dimethyl cyclopentene-4-propylene radical, 3,5-
4 dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl cyclopentene-4-
5 propylene radical, 2,3-dimethyl cyclopentene-4-propylene radical, 1,2,3-
6 trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-tetramethyl
7 cyclopentene-4-propylene radical.

8 11. The composition of claim 9, wherein the composition is an
9 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
10 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
11 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
12 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate
13 copolymer.

14 12. An oxygen scavenging composition comprising a polymeric backbone,
15 cyclic olefinic pendent groups, linking groups linking the olefinic pendent
16 groups to the polymeric backbone and a transition metal catalyst.

17 13. A composition according to claim 12, wherein the polymeric backbone is
18 ethylenic and the linking groups are selected from the group consisting
19 of:

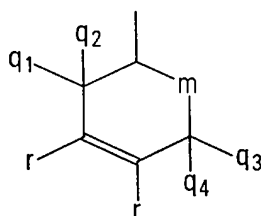
20 $-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;

21 $-(C=O)-NH-(-CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

22 wherein R is hydrogen or an alkyl group selected from the group
23 consisting of methyl, ethyl, propyl and butyl groups and where n is an
24 integer in the range from 1 to 12.

- 1 14. The composition of claim 12, wherein the cyclic olefinic pendent groups
2 have the structure (I):

3 (I)

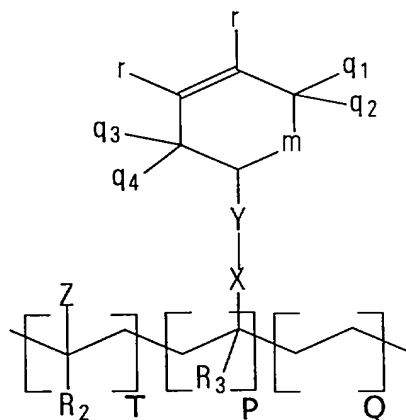


- 6
7 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$,
8 $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ with n being an integer in the
9 range from 0 to 4; and wherein, when r is $-H$, at least one of q_1 , q_2 , q_3
10 and q_4 is $-H$.

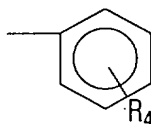
- 11 15. The composition of claim 12, wherein the polymeric backbone comprises
12 monomers selected from the group consisting of ethylene and styrene.
- 13 16. The composition of claim 12, wherein the cyclic olefinic pendent groups
14 are grafted onto the linking groups of the polymeric backbone by a
15 esterification, transesterification, amidation or transamidation reaction.
- 16 17. The composition of claim 16, wherein the esterification,
17 transesterification, amidation or transamidation reaction is a solution
18 reaction or a reactive extrusion.

- 1 18. The composition of claim 16, wherein the esterification,
 2 transesterification, amidation or transamidation reaction is catalyzed by
 3 a catalyst selected from the group consisting of strong non-oxidizing
 4 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
 5 Group IVA organometallics.
- 6 19. The composition of claim 18, wherein the catalyst is selected from a
 7 group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl
 8 titanate, tetraisopropyl titanate, tetra-n-propyl-titanate, tetraethyl titanate,
 9 2-hydroxy-pyridine and dibutyltin dilaurate.
- 10 20. The composition of claim 12, wherein the polymeric backbone, linking
 11 groups and cyclic olefin pendent groups comprise repeating units, each
 12 unit having a structure (II) as follows:

(II)



- 14
- 15 wherein P + T + Q is 100 mol % of the total composition; P is greater
 16 than 0 mol % of the total composition; Z is selected from the group
 17 consisting of an aryl group; -(C=O)OR₁; -O(C=O)R₁; and an alkyl aryl
 18 group:



- 1
- 2 where R₄ is selected from the group consisting of -CH₃, -C₂H₅, and -H;
- 3 R₁ is selected from the group consisting of -H, -CH₃, -C₂H₅, -C₃H₇ and
- 4 -C₄H₉; R₂ and R₃ are selected from the group consisting of -H and -CH₃;
- 5 X is selected from the group consisting of -O-, -NH-, -(C=O)O-,
- 6 -(C=O)NH-, -(C=O)S-, -O(C=O)- and -(CHR)_ℓ-; ℓ is an integer in the
- 7 range from 1 to 6; Y is -(CHR)_n-, where n is an integer in the range from
- 8 0 to 12; R being selected from the group consisting of -H, -CH₃ and
- 9 -C₂H₅; where q₁, q₂, q₃, q₄, and r are selected from the group consisting
- 10 of -H, -CH₃, and -C₂H₅; and where m is -(CH₂)_n- and where n is an
- 11 integer in the range from 0 to 4; and wherein when r is -H, at least one
- 12 of q₁, q₂, q₃ and q₄ is -H.
- 13 21. The composition of claim 20, wherein the cyclic olefinic pendent groups
- 14 are selected from the group consisting of cyclohexene-4-methylene
- 15 radical, 1-methyl cyclohexene-4-methylene radical, 2-methyl
- 16 cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-methylene
- 17 radical, 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl
- 18 cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-methylene
- 19 radical, 1,2,5-trimethyl cyclohexene-4-methylene radical, cyclohexene-4-
- 20 ethylene radical, 1-methyl cyclohexene-4-ethylene radical, 2-methyl
- 21 cyclohexene-4-ethylene radical, 5-methyl cyclohexene-4-ethylene
- 22 radical, 1,2-dimethyl cyclohexene-4-ethylene radical, 1,5-dimethyl
- 23 cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-ethylene
- 24 radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical, cyclohexene-4-
- 25 propylene radical, 1-methyl cyclohexene-4-propylene radical, 2-methyl
- 26 cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-propylene
- 27 radical, 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl

1 cyclohexene-4-propylene radical, 2,5-dimethyl cyclohexene-4-propylene
2 radical, 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-
3 methylene radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl
4 cyclopentene-4-methylene radical, 1,2-dimethyl cyclopentene-4-
5 methylene radical, 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-
6 dimethyl cyclopentene-4-methylene radical, 2,3-dimethyl cyclopentene-4-
7 methylene radical, 1,2,3-trimethyl cyclopentene-4-methylene radical,
8 1,2,3,5-tetramethyl cyclopentene-4-methylene radical, cyclopentene-4-
9 ethylene radical, 1-methyl cyclopentene-4-ethylene radical, 3-methyl
10 cyclopentene-4-ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene
11 radical, 3,5-dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl
12 cyclopentene-4-ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene
13 radical, 1,2,3-trimethyl cyclopentene-4-ethylene radical, 1,2,3,5-
14 tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-propylene
15 radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
16 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-
17 propylene radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-
18 dimethyl cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-
19 propylene radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and
20 1,2,3,5-tetramethyl cyclopentene-4-propylene radical.

21 22. The composition of claim 20, wherein the composition is an
22 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
23 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl
24 methyl methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
25 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate
26 copolymer.

27 23. The composition of claim 12, wherein odor and taste characteristics of
28 products packaged with material comprised of the composition are not
29 adulterated as a result of oxidation of the composition.

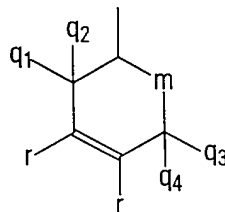
- 1 24. The composition of claim 12, wherein there is no significant
2 fragmentation of the olefinic pendent groups and linking groups from the
3 polymeric backbone as a result of oxidation of the composition.
- 4 25. The composition of claim 12, wherein the transition metal catalyst is a
5 metal salt.
- 6 26. The composition of claim 25, wherein the metal in the metal salt is
7 cobalt.
- 8 27. The composition according to claim 25, wherein the metal salt is
9 selected from the group consisting of cobalt neodecanoate, cobalt
10 2-ethylhexanoate, cobalt oleate and cobalt stearate.
- 11 28. The composition of claim 12, further comprising at least one triggering
12 material to enhance initiation of oxygen scavenging.
- 13 29. The composition of claim 28, wherein the triggering material is a photo
14 initiator.
- 15 30. An article of manufacture suitable as a container, the container inhibiting
16 oxidation of contents of the container by removing oxygen from the
17 container and by inhibiting ingress of oxygen into the container from
18 outside the container, wherein the article comprises an oxygen
19 scavenging composition which comprises a polymeric backbone, cyclic
20 olefinic pendent groups, linking groups linking the olefinic pendent
21 groups to the backbone, and a transition metal catalyst.
- 22 31. The article of manufacture of claim 30, wherein the polymeric backbone
23 is ethylenic and the linking groups are selected from the group
24 consisting of:
- 25 -O-(CHR)_n-; -(C=O)-O-(CHR)_n-; -NH-(CHR)_n-; -O-(C=O)-(CHR)_n-;

1 $-(C=O)-NH-(-CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

2 wherein R is hydrogen or an alkyl group selected from the group
3 consisting of methyl, ethyl, propyl and butyl groups and where n is an
4 integer in the range from 1 to 12.

5 32. The article of manufacture of claim 30, wherein the cyclic olefinic
6 pendent groups have the structure (I):

7 (I)

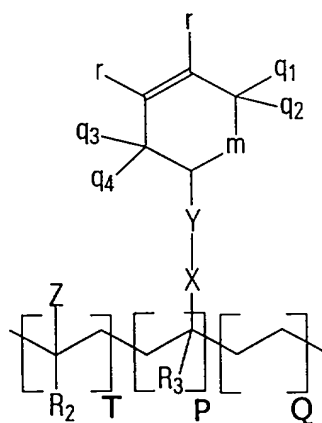


8
9 where q₁, q₂, q₃, q₄, and r are selected from the group consisting of -H,
10 -CH₃, and -C₂H₅; and where m is $-(CH_2)_n-$ and where n is an integer in
11 the range of from 0 to 4; and wherein when r is -H, at least one of q₁, q₂,
12 q₃ and q₄ is also -H.

13 33. The article of manufacture of claim 30, wherein the polymeric backbone
14 comprises monomers selected from the group consisting of ethylene and
15 styrene.

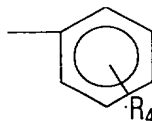
16 34. The article of manufacture of claim 30, wherein the cyclic olefinic
17 pendent groups are grafted onto the linking groups of the polymeric
18 backbone by a esterification, transesterification, amidation or
19 transamidation reaction.

- 1 35. The article of manufacture of claim 34, wherein the esterification,
2 transesterification, amidation or transamidation reaction is a solution
3 reaction or a reactive extrusion.
- 4 36. The article of manufacture of claim 34, wherein the esterification,
5 transesterification, amidation or transamidation reaction is catalyzed by
6 a catalyst selected from the group consisting of strong non-oxidizing
7 acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and
8 Group IVA organometallics.
- 9 37. The article of manufacture of claim 36, wherein the catalyst is selected
10 from the group consisting of toluene sulfonic acid, sodium methoxide,
11 tetrabutyl titanate, tetraisopropyl titanate, tetra-n-propyl-titanate,
12 tetraethyl titanate, 2-hydroxy-pyridine and dibutyltin dilaurate.
- 13 38. The article of manufacture of claim 30, wherein the backbone, linking
14 groups and cyclic olefin pendent groups comprise repeating units, each
15 unit having a structure (II) as follows:



(II)

1 wherein P+T + Q is 100 mol % of the total composition; P is greater than
2 0 mol % of the total composition; Z is selected from the group consisting
3 of an aryl group, $-(C=O)OR_1$, $-O(C=O)R_1$ and an alkyl aryl group:



4

5 where R₄ is selected from the group consisting of $-CH_3$, $-C_2H_5$, and $-H$;
6 R₁ is selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$ and
7 $-C_4H_9$; R₂ and R₃ are selected from the group consisting of $-H$ and CH_3 ;
8 X is selected from the group consisting of $O-$, $-NH-$, $-(C=O)O-$,
9 $-(C=O)NH-$, $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell-$; ℓ is an integer selected
10 from the group consisting of 1, 2, 3, 4, 5 and 6; Y is $-(CHR)_n-$, where n is
11 an integer in the range from 0 to 12 and R is selected from the group
12 consisting of $-H$, $-CH_3$ and C_2H_5 ; and where q₁, q₂, q₃, q₄, and r are
13 selected from the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m
14 is $-(CH_2)_n-$ and where n is an integer in the range of from 0 to 4; and
15 wherein when r is $-H$, at least one of q₁, q₂, q₃, and q₄ is $-H$.

- 16 39. The article of manufacture of claim 30, wherein the cyclic olefinic
17 pendent groups are selected from the group consisting of cyclohexene-
18 4-methylene radical, 1-methyl cyclohexene-4-methylene radical,
19 2-methyl cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-
20 methylene radical, 1,2-dimethyl cyclohexene-4-methylene radical,
21 1,5-dimethyl cyclohexene-4-methylene radical, 2,5-dimethyl
22 cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-
23 methylene radical, cyclohexene-4-ethylene radical, 1-methyl
24 cyclohexene-4-ethylene radical, 2-methyl cyclohexene-4-ethylene
25 radical, 5-methyl cyclohexene-4-ethylene radical, 1,2-dimethyl

- 1 cyclohexene-4-ethylene radical, 1,5-dimethyl cyclohexene-4-ethylene
2 radical, 2,5-dimethyl cyclohexene-4-ethylene radical, 1,2,5-trimethyl
3 cyclohexene-4-ethylene radical, cyclohexene-4-propylene radical,
4 1-methyl cyclohexene-4-propylene radical, 2-methyl cyclohexene-4-
5 propylene radical, 5-methyl cyclohexene-4-propylene radical,
6 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl
7 cyclohexene-4-propylene radical, 2,5-dimethyl cyclohexene-4-propylene
8 radical, 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-
9 4-methylene radical, 1-methyl cyclopentene-4-methylene radical,
10 3-methyl cyclopentene-4-methylene radical, 1,2-dimethyl cyclopentene-
11 4-methylene radical, 3,5-dimethyl cyclopentene-4-methylene radical,
12 1,3-dimethyl cyclopentene-4-methylene radical, 2,3-dimethyl
13 cyclopentene-4-methylene radical, 1,2,3-trimethyl cyclopentene-4-
14 methylene radical, 1,2,3,5-tetramethyl cyclopentene-4-methylene
15 radical, cyclopentene-4-ethylene radical, 1-methyl cyclopentene-4-
16 ethylene radical, 3-methyl cyclopentene-4-ethylene radical, 1,2-dimethyl
17 cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-ethylene
18 radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
19 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-
20 ethylene radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical,
21 cyclopentene-4-propylene radical, 1-methyl cyclopentene-4-propylene
22 radical, 3-methyl cyclopentene-4-propylene radical, 1,2-dimethyl
23 cyclopentene-4-propylene radical, 3,5-dimethyl cyclopentene-4-
24 propylene radical, 1,3-dimethyl cyclopentene-4-propylene radical,
25 2,3-dimethyl cyclopentene-4-propylene radical, 1,2,3-trimethyl
26 cyclopentene-4-propylene radical, and 1,2,3,5-tetramethyl
27 cyclopentene-4-propylene radical.
- 28 40. The article of manufacture of claim 30, wherein the composition is an
29 ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a
30 cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl
31 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate

- 1 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate
2 copolymer.
- 3 41. The article of manufacture according to claim 30, wherein the transition
4 metal catalyst is a metal salt.
- 5 42. The article of manufacture according to claim 41, wherein the metal in
6 the metal salt is cobalt.
- 7 43. The article of manufacture of according to claim 41, wherein the metal
8 salt is selected from the group consisting of cobalt neodecanoate, cobalt
9 2-ethylhexanoate, cobalt oleate and cobalt stearate.
- 10 44. The article of manufacture of claim 30, further comprising at least one
11 triggering material to enhance initiation of oxygen scavenging.
- 12 45. The article of manufacture of claim 44, wherein the triggering material is
13 a photoinitiator.
- 14 46. The article of manufacture of claim 30, wherein odor and taste
15 characteristics of products packaged with material comprised of the
16 composition are not adulterated as a result of oxidation of the
17 composition.
- 18 47. The article of manufacture of claim 30, wherein there is no significant
19 fragmentation of the olefinic pendent groups and linking groups from the
20 polymeric backbone as a result of oxidation of the composition.
- 21 48. The article of manufacture of claim 30 wherein the article is a package.
- 22 49. The article of manufacture of claim 48, wherein the package comprises a
23 flexible film having a thickness of at most 10 mil or a flexible sheet
24 having a thickness of at least 10 mil.

- 1 50. The article of manufacture of claim 48, wherein the oxygen scavenging
2 system of the package comprises at least one additional layer selected
3 from among oxygen barrier layers, polymeric selective layers, and heat
4 seal layers.
- 5 51. The article of manufacture of claim 48, wherein the article is a package
6 with a food product located within the package.
- 7 52. The article of manufacture of claim 48, wherein the article is a package
8 for packaging a cosmetic, chemical, electronic device, pesticide or a
9 pharmaceutical composition.
- 10 53. A multi-layer film comprising the article of manufacture according to
11 claim 30, and at least one additional functional layer.
- 12 54. The multi-layer film according to claim 53, wherein at least one
13 additional layer is selected from among oxygen barrier layers, polymeric
14 selective barrier layers, structural layers and heat seal layers.
- 15 55. The multi-layer film according to claim 53, wherein the at least one
16 additional layer is an oxygen barrier layer.
- 17 56. The multi-layer film according to claim 55, further comprising at least one
18 polymeric selective barrier layer.
- 19 57. The multi-layer film according to claim 55, further comprising at least one
20 heat seal layer.
- 21 58. The multi-layer film according to claim 55, further comprising at least one
22 structural layer.

- 1 59. The article of claim 30, wherein the article is a rigid container, sealing
2 gasket, patch, container closure device, bottle cap, bottle cap insert or
3 molded or thermoformed shape.
- 4 60. The article of claim 59, wherein the molded or thermoformed shape is a
5 bottle or tray.
- 6 61. A layer suitable for scavenging oxygen comprising:
- 7 (a) a polymer backbone;
- 8 (b) cyclic olefinic pendent groups;
- 9 (c) linking groups linking the backbone with the pendent groups; and
- 10 (d) a transition metal catalyst.
- 11 62. The layer of claim 61, wherein odor and taste characteristics of products
12 packaged with material comprised of the layer are not adulterated as a
13 result of oxidation of the layer.
- 14 63. The layer of claim 61, wherein there is no significant fragmentation of the
15 olefinic pendent groups and linking groups from the polymeric backbone
16 as a result of oxidation of the layer.
- 17 64. A layer according to claim 61, wherein the transition metal catalyst is a
18 metal salt.
- 19 65. A layer according to claim 64, wherein the transition metal in the metal
20 salt is cobalt.

- 1 66. A layer according to claim 64, wherein the metal salt selected from the
2 group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate,
3 cobalt oleate and cobalt stearate.
- 4 67. A layer according to claim 61, wherein said layer in addition comprises
5 polymeric diluent.
- 6 68. A layer according to claim 67, wherein said diluent is a thermoplastic
7 polymer.
- 8 69. A layer according to claim 61, wherein said layer is adjacent to one or
9 more additional layers.
- 10 70. A layer according to claim 69, wherein at least one additional layer is an
11 oxygen barrier.
- 12 71. A layer according to claim 70, wherein said oxygen barrier comprises a
13 member of the group consisting of poly(ethylene-vinyl alcohol),
14 polyacrylonitrile, poly(vinyl chloride), polyamides, poly(vinylidene
15 dichloride), poly(ethylene terephthalate), silica, metal foil and metalized
16 polymeric films.
- 17 72. A layer according to claim 69, wherein one or more of said additional
18 layer or layers is coextruded with said layer.
- 19 73. A layer according to claim 69, wherein one or more of said additional
20 layer or layers is laminated onto said layer.
- 21 74. A layer according to claim 69, wherein one or more of said additional
22 layer or layers is coated onto said layer.
- 23 75. A layer according to claim 69, wherein said layer is flexible.

- 1 76. A layer according to claim 69, wherein said layer is transparent.
- 2 77. An article for packaging wherein the article comprises a layer according
3 to claim 61.
- 4 78. A process of making a polymer material by a process selected from the
5 group consisting of esterification, transesterification, amidation,
6 transamidation and direct polymerization, wherein the polymer material
7 comprises a polymer backbone, cyclic olefinic pendent groups, linking
8 groups linking the backbone with the pendent groups.
- 9 79. The process of claim 78, wherein making the polymer material
10 comprises the steps of:
- 11 (a) selecting polymers from the group consisting of styrene/maleic
12 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
13 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
14 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
15 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl
16 acrylate, and styrene/methyl methacrylate to form a mixture and
17 combining the polymers with a esterifying/transesterifying
18 compound selected from the group consisting of cyclohexene-4-
19 methanol, 1-methyl cyclohexene-4-methanol, 2-methyl
20 cyclohexene-4-methanol, 5-methyl cyclohexene-4-methanol, 1,2-
21 dimethyl cyclohexene-4-methanol, 1,5-dimethyl cyclohexene-4-
22 methanol, 2,5-dimethyl cyclohexene-4-methanol, 1,2,5-trimethyl
23 cyclohexene-4-methanol, cyclohexene-4-ethanol, 1-methyl
24 cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol, 5-methyl
25 cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol, 1,5-
26 dimethyl cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-
27 ethanol, 1,2,5-trimethyl cyclohexene-4-ethanol, cyclohexene-4-
28 propanol, 1-methyl cyclohexene-4-propanol, 2-methyl cyclohexene-

- 1 4-propanol, 5-methyl cyclohexene-4-propanol, 1,2-dimethyl
2 cyclohexene-4-propanol, 1,5-dimethyl cyclohexene-4-propanol,
3 2,5-dimethyl cyclohexene-4-propanol, 1,2,5-trimethyl cyclohexene-
4 4-propanol, cyclopentene-4-methanol, 1-methyl cyclopentene-4-
5 methanol, 3-methyl cyclopentene-4-methanol, 1,2-dimethyl
6 cyclopentene-4-methanol, 3,5-dimethyl cyclopentene-4-methanol,
7 1,3-dimethyl cyclopentene-4-methanol, 2,3-dimethyl cyclopentene-
8 4-methanol, 1,2,3-trimethyl cyclopentene-4-methanol, 1,2,3,5-
9 tetramethyl cyclopentene-4-methanol, cyclopentene-4-ethanol, 1-
10 methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-ethanol,
11 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl cyclopentene-4-
12 ethanol, 1,3-dimethyl cyclopentene-4-ethanol, 2,3-dimethyl
13 cyclopentene-4-ethanol, 1,2,3-trimethyl cyclopentene-4-ethanol,
14 1,2,3,5-tetramethyl cyclopentene-4-ethanol, cyclopentene-4-
15 propanol, 1-methyl cyclopentene-4-propanol, 3-methyl
16 cyclopentene-4-propanol, 1,2-dimethyl cyclopentene-4-propanol,
17 3,5-dimethyl cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-
18 4-propanol, 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl
19 cyclopentene-4-propanol, and 1,2,3,5-tetramethyl cyclopentene-4-
20 propanol;
- 21 (b) heating the polymers and esterifying/transesterifying compounds
22 selected in (a) to form a polymer melt;
- 23 (c) processing the melt in an extruder under
24 esterification/transesterification conditions with
25 esterification/transesterification catalysts and antioxidants
26 protecting the melt from oxidation during extrusion, so that the
27 polymer melt undergoes esterification of polymeric anhydrides with
28 cyclic olefin pendent groups, esterification of polymeric acids with
29 cyclic olefin pendent groups or exchange of alkyl groups of
30 polymeric esters with cyclic olefin pendent groups; and

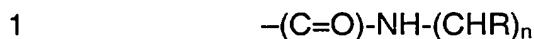
1 (d) removing volatile organic products and by-products from the melt.

2 80. The process of claim 78, wherein making the polymer material
3 comprises the steps of:

4 (a) selecting polymers from the group consisting of styrene/maleic
5 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
6 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
7 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
8 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl
9 acrylate, and styrene/methyl methacrylate to form a mixture and
10 combining the polymers with a amidizing/transamidizing compound
11 selected from the group consisting of cyclohexene-4-methyl amine,
12 1-methyl cyclohexene-4-methyl amine, 2-methyl cyclohexene-4-
13 methyl amine, 5-methyl cyclohexene-4-methyl amine, 1,2-dimethyl
14 cyclohexene-4-methyl amine, 1,5-dimethyl cyclohexene-4-methyl
15 amine, 2,5-dimethyl cyclohexene-4-methyl amine, 1,2,5-trimethyl
16 cyclohexene-4-methyl amine, cyclohexene-4-ethyl amine, 1-methyl
17 cyclohexene-4-ethyl amine, 2-methyl cyclohexene-4-ethyl amine,
18 5-methyl cyclohexene-4-ethyl amine, 1,2-dimethyl cyclohexene-4-
19 ethyl amine, 1,5-dimethyl cyclohexene-4-ethyl amine, 2,5-dimethyl
20 cyclohexene-4-ethyl amine, 1,2,5-trimethyl cyclohexene-4-ethyl
21 amine, cyclohexene-4-propyl amine, 1-methyl cyclohexene-4-
22 propyl amine, 2-methyl cyclohexene-4-propyl amine, 5-methyl
23 cyclohexene-4-propyl amine, 1,2-dimethyl cyclohexene-4-propyl
24 amine, 1,5-dimethyl cyclohexene-4-propyl amine, 2,5-dimethyl
25 cyclohexene-4-propyl amine, 1,2,5-trimethyl cyclohexene-4-propyl
26 amine, cyclopentene-4-methyl amine, 1-methyl cyclopentene-4-
27 methyl amine, 3-methyl cyclopentene-4-methyl amine, 1,2-dimethyl
28 cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl
29 amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl
30 cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-

- 1 methyl amine, 1,2,3,5-tetramethyl cyclopentene-4-methyl amine,
2 cyclopentene-4-ethyl amine, 1-methyl cyclopentene-4-ethyl amine,
3 3-methyl cyclopentene-4-ethyl amine, 1,2-dimethyl cyclopentene-4-
4 ethyl amine, 3,5-dimethyl cyclopentene-4-ethyl amine,
5 1,3-dimethyl cyclopentene-4-ethyl amine, 2,3-dimethyl
6 cyclopentene-4-ethyl amine, 1,2,3-trimethyl cyclopentene-4-ethyl
7 amine, 1,2,3,5-tetramethyl cyclopentene-4-ethyl amine,
8 cyclopentene-4-propyl amine, 1-methyl cyclopentene-4-propyl
9 amine, 3-methyl cyclopentene-4-propyl amine, 1,2-dimethyl
10 cyclopentene-4-propyl amine, 3,5-dimethyl cyclopentene-4-propyl
11 amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-dimethyl
12 cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-
13 propyl amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl
14 amine;
- 15 (b) heating the polymers and amidizing/transamidizing compounds
16 selected in (a) to form a polymer melt;
- 17 (c) processing the melt in an extruder under amidation/transamidation
18 conditions with amidation/transamidation catalysts and antioxidants
19 protecting the melt from oxidation during extrusion, so that the
20 polymer melt undergoes amidation of polymeric anhydrides with
21 cyclic olefin pendent groups, amidation of polymeric acids with
22 cyclic olefin pendent groups or exchange of alkyl groups of
23 polymeric esters with cyclic olefin pendent groups; and
- 24 (d) removing volatile organic products and by-products from the melt.
- 25 81. The process of claim 78, wherein the making of the polymer material
26 comprises the steps of:

- 1 (a) adding to an autoclave, ethylene and a vinyl monomer comprising
2 a pendent cyclohexene;
- 3 (b) stirring the ethylene and the vinyl monomer in the autoclave to
4 achieve a mixture;
- 5 (c) adding a polymerization initiator before, during or after the stirring
6 step;
- 7 (d) polymerizing the mixture to achieve a polymer; and
- 8 (e) isolating and purifying the polymer.
- 9 82. The process of claim 81, wherein in step (a) an alpha-olefin is added to
10 the autoclave along with the ethylene and the vinyl monomer and in
11 step (b) the alpha-olefin is stirred with the ethylene and the vinyl
12 monomer to achieve the mixture.
- 13 83. The process of claim 79, wherein the polymeric backbone is ethylenic
14 and the linking groups are selected from the group consisting of:
- 15 $-\text{O}-(\text{CHR})_n-; -(\text{C}=\text{O})-\text{O}-(\text{CHR})_n-; -\text{NH}-(\text{CHR})_n-;$
- 16 $-\text{O}-(\text{C}=\text{O})-(\text{CHR})_n-; -(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n-;$ and
- 17 $-(\text{C}=\text{O})-\text{O}-\text{CHOH}-\text{CH}_2-\text{O}-;$
- 18 where R is hydrogen or an alkyl group selected from the group
19 consisting of methyl, ethyl, propyl and butyl groups and where n is an
20 integer in the range from 1 to 12.
- 21 84. The process of claim 80, wherein the polymeric backbone is ethylenic
22 backbone and the linking group is:



2 where R is hydrogen or an alkyl group selected from the group
3 consisting of methyl, ethyl, propyl and butyl groups and where n is an
4 integer in the range from 1 to 12.

5 85. The process of claim 78, wherein the material is an oxygen scavenging
6 composition further comprising a transition metal catalyst.

7 86. The process of claim 85, wherein the transition metal catalyst is a metal
8 salt.

9 87. The process of claim 86, wherein the metal in the metal salt is cobalt.

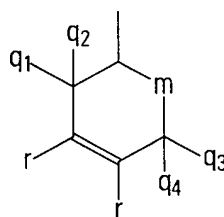
10 88. The process according to claim 86, wherein the metal salt is selected
11 from the group consisting of cobalt neodecanoate, cobalt
12 2-ethylhexanoate, cobalt oleate and cobalt stearate.

13 89. The process of claim 85, wherein the oxygen scavenging composition
14 further comprises at least one triggering material to enhance initiation of
15 oxygen scavenging.

16 90. The process of claim 89, wherein the triggering material is a
17 photoinitiator.

18 91. The process of claim 78, wherein the cyclic olefinic pendent groups have
19 the structure (I):

(I)



where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ and where n is an integer in the range of from 0 to 4; and wherein when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is $-H$.

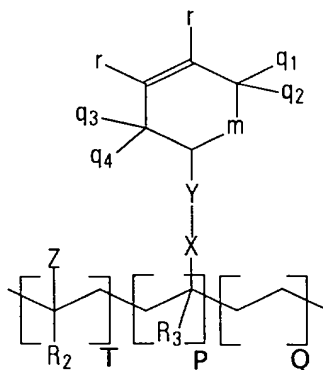
92. The process of claim 78, wherein the functional groups with attached cyclic olefinic pendent groups are grafted onto the linking backbone by a esterification, transesterification, amidation or transamidation reaction.

93. The process of claim 78, wherein the reaction is a solution reaction or a reactive extrusion.

94. The process of claim 78, wherein the esterification, transesterification, amidation or transamidation reaction is catalyzed by a catalyst selected from the group consisting of strong non-oxidizing acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, Group IVA organometallics.

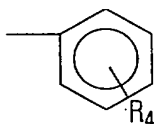
95. The process of claim 94, wherein the catalyst is selected from the group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl titanate, tetraisopropyl titanate, tetra-*n*-propyl-titanate, tetraethyl titanate, 2-hydroxy-pyridine and dibutyltin dilaurate.

- 1 96. The process of claim 78, wherein the backbone, linking groups and
 2 cyclic olefin pendent groups comprise repeating units, each unit having a
 3 structure (II) as follows:



(II)

- 4
 5 wherein P + T + Q is 100 mol % of the total composition; P is greater
 6 than 0; Z is selected from the group consisting of an aryl group,
 7 $-(C=O)OR_1$, $-O(C=O)R_1$ and an alkyl aryl group:



- 8
 9 where R_4 is selected from the group consisting of $-H$, $-CH_3$ and $-C_2H_5$; R_1
 10 is selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_5$ and
 11 $-C_4H_7$; R_2 and R_3 is selected from the group consisting of $-H$ and CH_3 ; X
 12 is selected from the group consisting of $O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$,
 13 $-(C=O)S-$, $-O(C=O)-$ and $-(CHR)_\ell$; ℓ is an integer selected from the
 14 group consisting of 1, 2, 3, 4, 5 and 6; Y is $-(CHR)_n$, where n is an
 15 integer in the range from 0 to 12 where R is selected from the group
 16 consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected

1 from the group consisting of -H, -CH₃, and -C₂H₅; and where m is
2 -(CH₂)_n- and where n is an integer in the range of from 0 to 4; and
3 wherein when r is -H, at least one of q₁, q₂, q₃ and q₄ is -H.

- 4 97. The process of claim 78, wherein the cyclic olefinic pendent groups are
5 selected from the group consisting of cyclohexene-4-methylene radical,
6 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-
7 methylene radical, 5-methyl cyclohexene-4-methylene radical,
8 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl
9 cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-
10 methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical,
11 cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene
12 radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl cyclohexene-
13 4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical,
14 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-
15 4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical,
16 cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene
17 radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl
18 cyclohexene-4-propylene radical, 1,2-dimethyl cyclohexene-4-propylene
19 radical, 1,5-dimethyl cyclohexene-4-propylene radical, 2,5-dimethyl
20 cyclohexene-4-propylene radical, 1,2,5-trimethyl cyclohexene-4-
21 propylene radical, cyclopentene-4-methylene radical, 1-methyl
22 cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-methylene
23 radical, 1,2-dimethyl cyclopentene-4-methylene radical, 3,5-dimethyl
24 cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
25 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical,
26 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
27 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical,
28 1-methyl cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-
29 ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene radical,
30 3,5-dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl
31 cyclopentene-4-ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene

1 radical, 1,2,3-trimethyl cyclopentene-4-ethylene radical,
2 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
3 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
4 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-
5 propylene radical, 3,5-dimethyl cyclopentene-4-propylene radical,
6 1,3-dimethyl cyclopentene-4-propylene radical, 2,3-dimethyl
7 cyclopentene-4-propylene radical, 1,2,3-trimethyl cyclopentene-4-
8 propylene radical, and 1,2,3,5-tetramethyl cyclopentene-4-propylene
9 radical.

10 98. The process of claim 78, wherein the composition is a ethylene/methyl
11 acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl
12 acrylate/ethylene copolymer, a cyclohexenyl methyl
13 methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate
14 homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate
15 copolymer.

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ABSTRACT OF THE DISCLOSURE

- 2 A family of polymers containing selected cyclic allylic pendent groups for
3 oxygen scavenging packaging which has minimal organoleptic by-products
4 after oxidation.

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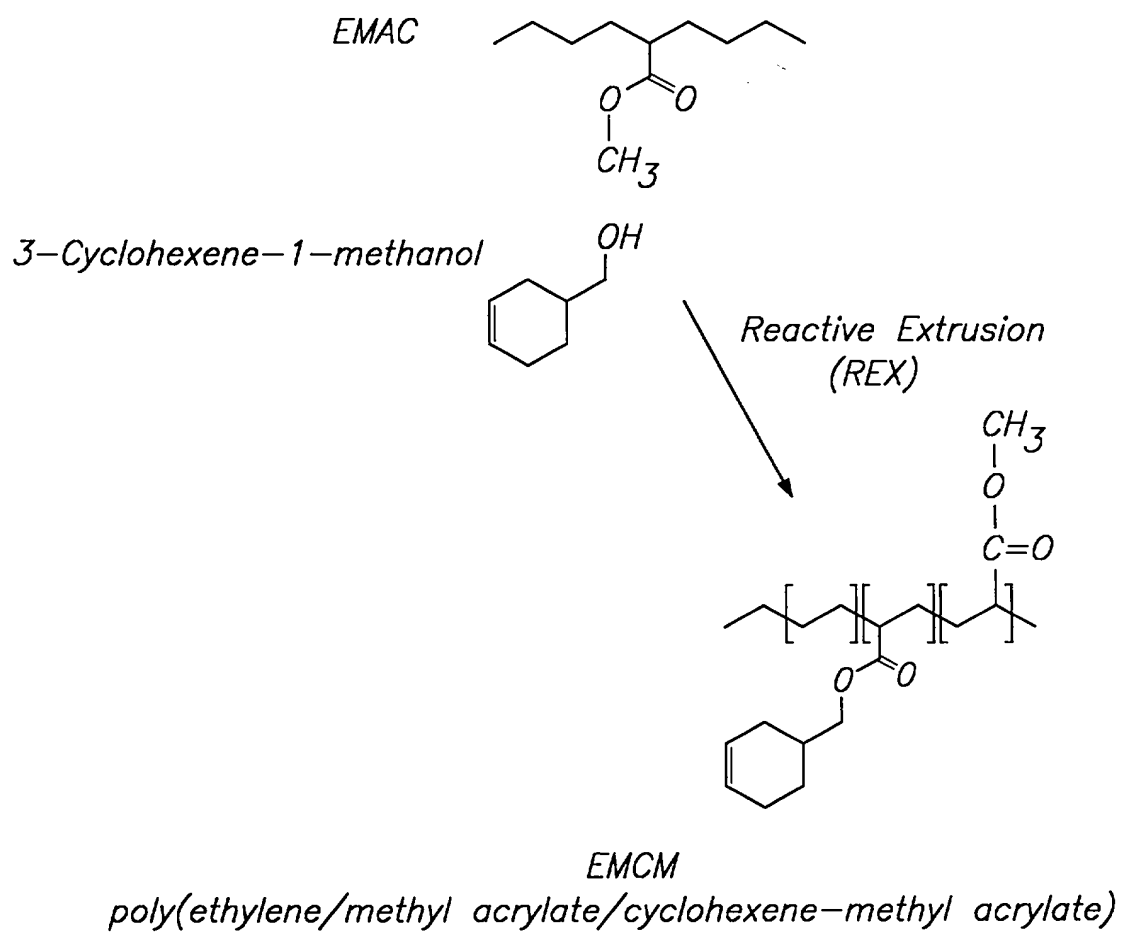


FIG. 1

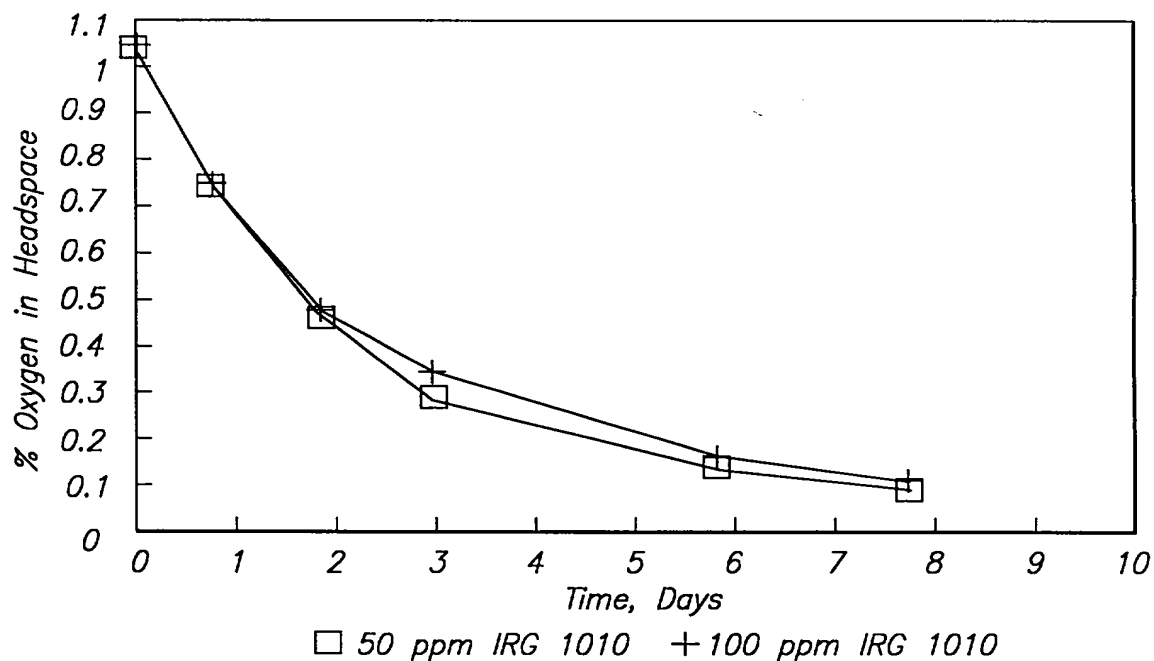


FIG. 2

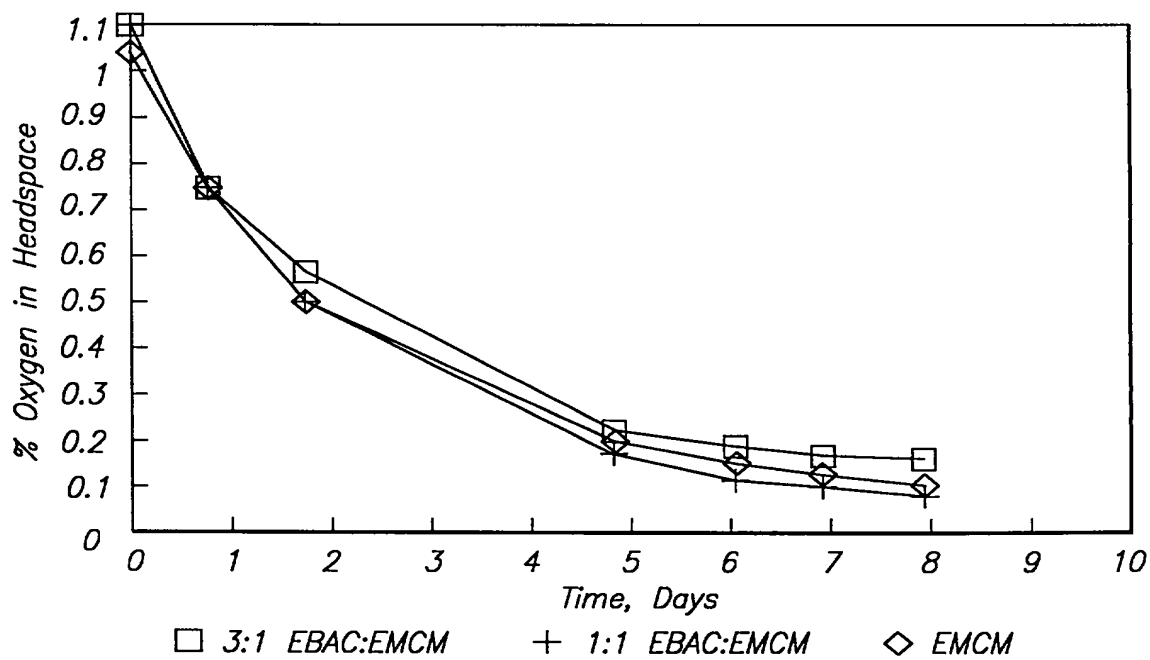


FIG. 3



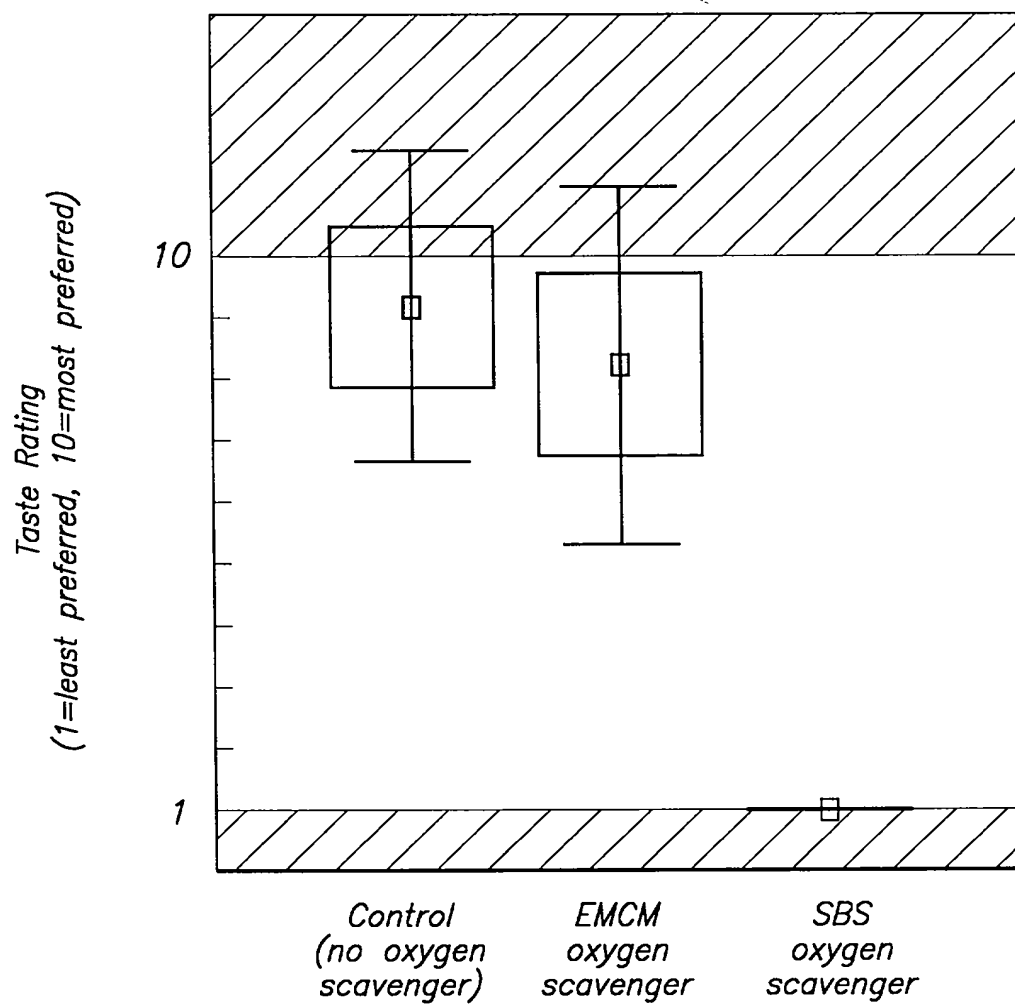
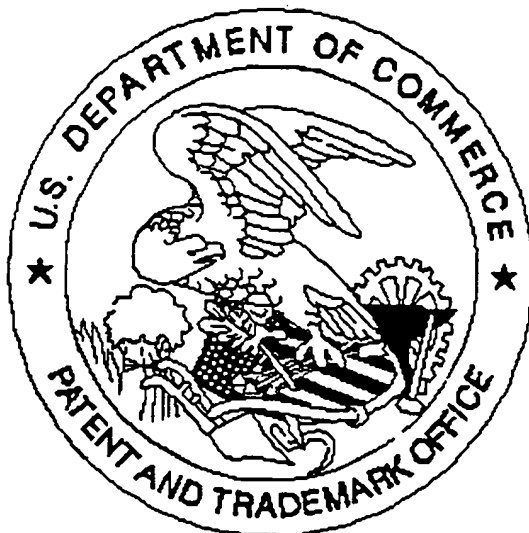


FIG. 5

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